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ScienceDirect

Energy Procedia 126 (201709) 1075–1082

Energy Procedia

www.elsevier.com/locate/procedia

72nd Conference of the Italian Thermal Machines Engineering Association, ATI2017, 6-8 September 2017, Lecce, Italy

Numerical Optimization of SPR Sensors for Lube Oil Real-Time Optical Characterization in Large 2-Stroke Marine Diesel Engines

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Abstract

Lubrication of large two stroke marine diesel engines typically is performed by specially blended lubricants with high $CaCO_3$ concentration in order to prevent sulphuric acid corrosion. The feed rate of lubricant, which is injected into the engine, is strictly related to neutralization reaction of sulphuric acid. At the state of the art, its amount is established following a function of engine load and sulphur content of fuel oil, but regardless the stoichiometric quantity needed to neutralize acid corrosion effects. As result of this lubrication strategy, feed rate of lubricant often results higher than the minimum stoichiometric quantity, yielding unnecessary costs, but sometimes feed rate of lubricant and its content of $CaCO_3$ cannot be enough to completely neutralize sulphuric acid, producing corrosion. Taking into account that concentration of $CaCO_3$ within lube oil can be estimated by measuring refractive index, this work aimed to study *SPR* sensors, capable to measure in real time small variation of lubricant optical properties, in order to adjust lubricant feed rate, according to the real needs of neutralization. Therefore, a numerical optimization of SPR sensors for lube oil characterization has been carried out, analysing several cases, different for laser source, optical prism and thickness of 3 metal film layers. Mathematical results allowed to find the best sensor in terms of sensitivity. This work is the first step towards the development of a semi-closed loop lubrication control system.

Peer-review under responsibility of the scientific committee of the 72nd Conference of the Italian Thermal Machines Engineering Association

Keywords: Lubricant; SPR sensor; Numerical optimization.

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Peer-review under responsibility of the scientific committee of the 72nd Conference of the Italian Thermal Machines Engineering Association
10.1016/j.egypro.2017.08.238

Nomenclature

c	velocity of light;
k_{sp}	wave vector;
n	refractive index;
ε_m	permittivity of the metallic film;
ε_d	permittivity of dielectric;
ω	angular frequency;
θ	angle.

1. Introduction

Large two stroke marine diesel engines are the prime movers for a vast majority of today's merchant shipping for reasons such as superior thermal efficiency compared to other propulsion systems and the ability to burn residual fuel oil, the latter resulting in combustion of high Sulphur contents of the fuels. The International Maritime Organization, IMO, has therefore introduced a Sulphur cap of 3.5% for ocean going vessels in 2012 and has limited the Sulphur content for Emission Controlled Areas, IMO-SECA, from 1.5% to 1% in 2010. The primary target of this regulation is to reduce SO_x exhaust gas emissions for environmental reasons. Such levels of fuel sulphur content challenge engine manufacturers not only from the emission abatement technology, but also from the tribology point of view.

Sulphur related combustion products react with humidity of combustion air to form sulphuric acid, which considerably affects lifetime performance of such an engine. Therefore, specially blended lubricants with a high alkaline reserve are used to prevent sulphuric acid from corroding the cylinder. At the state of the art, their amount is established regardless the stoichiometric quantity needed to neutralize acid corrosion, which actually can be estimated by means of the residual amount of $CaCO_3$ within lube oil. As result of this lubrication strategy, feed rate of lubricant, in some cases, can be higher than the stoichiometric quantity, producing unnecessary costs, while in opposite situations feed rate of lubricant cannot be enough to completely neutralize sulphuric acid, yielding corrosion.

Optimizing lifetime performance of large two stroke marine diesel engines, hence, comprehends maximizing reliability and simultaneously optimizing the utilization of the lubricant. According to the latter target, this work is focused on development and optimization of a near real time monitoring sensor, able to characterize relevant lubricant properties.

According to this target, in the last years, researchers have developed several methods for detecting oil degradation. Jagannathan and Raju [1] carried out a study to predict quality and technical life of engine oils, for industrial and automotive applications. Youngk *et al.* [2], in order to define the best intervals of oil change, demonstrated that too frequent oil change can reduce engine lifetime expectancy because of their additives, which can accelerate chemical wear of engine surfaces. Stelmaszewski and Kròl [3] studied the relationship between the wear degree of oil and the change of its optical properties, by means of optical methods, as fluorescence, light absorption, light refraction. J. Fall [4] and M.A. Al-Ghouti [5] used chromatographic and spectroscopic techniques respectively, in the examination of engine oils. Owrang *et al.* [6] studied the relationship between formation of combustion chamber deposits and engine oil composition.

Recently, some sensors, able to measure in real-time physical and/or chemical properties of lubricants, which can be used as indicators for their deterioration, e.g. viscosity, permittivity or infrared absorption have been studied [6]. For example, J. Edmond [7] investigated optical methods of scattering counters, to detect small particles in lubricating oil during its aging. Other researchers proposed to measure oil viscosity by means of piezoelectric materials [8], or infrared analysis to detect several oil components, as well as many contaminants in the oil like soot, water, glycol and unburned fuel [9].

Differently from the above-cited works, in this paper, numerical simulations have been performed in order to define the best configuration of a SPR sensor, able to analyze in real-time lube oil for large two stroke marine engine. Particularly, taking into account that concentration of $CaCO_3$ within lube oil can be used as indicator of neutralization reactions, several sensors, different for laser source, optical prism and thickness of 3 metal film layers, have been numerically studied, to find the best solution in terms of sensitivity, able to detect small variation of lube oil refractive index due to change in $CaCO_3$ concentration.

2. Lubricants for large two stroke diesel engines

A typical lubrication system of a large two stroke marine diesel engines consists of a lubricant tank, a filter system, lubricant dosage pumps and lubricant injectors. Besides, the tribosystem, consisting of piston rings, cylinder liner and lubricant, is designed to evenly distribute the lubricant on the cylinder wall in order to perform obvious functions like sealing the combustion chamber against the piston underside, to reduce friction and besides this, the most important purpose, to neutralize combustion products like sulphuric acid impinging on the cylinder wall. In order to optimize the utilization of the lubricants neutralization capabilities, lubrication feed rates are adjusted following a function of engine load and sulphur content of fuel oil, but it is independent from the real formation/neutralization reactions of sulphuric acid within combustion chamber.

Lubrication of large two stroke diesel engines typically is performed on a total loss basis. After lubricating the piston ring – cylinder – interface, much of the lubricant is lost either in the combustion chamber, where it is removed through the exhaust system, or during the scavenging process, where the lubricant expands into the scavenge air receiver. Therefore, it is important to develop a real-time sensor, able to characterize relevant lubricant properties, to correct the lubricant feed rate according to the real necessity of neutralization, thus providing the basics towards the development of a semi-closed loop lubrication control system.

2.1. Chemical reactions of sulphuric acid formation, corrosion effects and neutralization

Investigations in the context of this work focus on neutralization of sulphuric acid by means of $CaCO_3$. A typical two-stroke marine diesel engine lubricant is characterized by its total base number, TBN. TBN is expressed in terms of the equivalent number of milligrams of potassium hydroxide per gram of oil sample (mg KOH / g) and describes the capability to neutralize an equivalent amount of acid. TBN concentrations in the marine industry typically range from TBN 20 up to TBN 100 depending of the fuel Sulphur content.

Once sulphuric acid gets in contact with the lubricant film, the neutralization reaction is initiated instantly when H_2SO_4 molecules collide with $CaCO_3$ molecules.

The neutralization reaction mechanism follows:

$$H_2SO_4 + CaCO_3 + H_2O \longrightarrow CaSO_4 * 2H_2O + CO_2 \quad (1)$$

As neutralization of sulphuric acid reduces the concentration of $CaCO_3$, the residual concentration of $CaCO_3$ directly indicates the depletion of the lubricant. Hence, $CaCO_3$ concentrations in the residual lubricant can be considered an appropriate parameter to determine lubricant degradation.

A commonly used approach in characterizing TBN is the application of titration methods according to the American Society for Testing and Materials (ASTM). ASTM D2896-11 standard methods make use of standardized acids to titrate all basic constituents in a lubricant. These methods are very accurate, but time consuming and must be performed in a laboratory. Instead of titration methods, infrared spectroscopy has established as a useful tool to quantify TBN. IR spectroscopy uses a radiative source and a detector to investigate the interaction of matter and light and therewith detect variations of TBN by changes of the IR spectrum. A shortcoming of the latter approach however excludes sooty lubricant samples from a proper determination of TBN. An outcome of this particular approach reveals the dependency of light and the optical properties of a lubricant, which results in a detailed investigation on this topic as a fundamental part of this work.

Having identified residual $\mathrm{CaCO_3}$ concentrations of the lubricant as main indicator of lubricant degradation leads to the logical approach of utilizing specially blended analytes as reference. The analyte, involved in this investigation, is a standard mineral base oil differing in concentrations of $\mathrm{CaCO_3}$. Concentrations of $\mathrm{CaCO_3}$ allow to simulate Total Base Number (BN) variations of a representative marine engine lubricant. Typical values in practice range from BN 20 to BN 100, which corresponds to concentrations of 11.2 mg/g (or ‰) of $\mathrm{CaCO_3}$ and 56.1 mg/g (or ‰) of $\mathrm{CaCO_3}$

respectively. Accurately metered amounts of $CaCO_3$ are added to a reference base oil to obtain samples with representative quantities.

Table 1 gives an overview on the investigated analytes and related concentrations of $CaCO_3$, the corresponding total base number (BN) and related refractive indices.

Table 1. Overview of investigated analytes.

Analyte sample number	TBN [mgKOH/g]	$CaCO_3$ [mg/g]	Refractive index [RIU]
1	0	0	1.486
2	20	11.2	1.488
3	40	22.4	1.489
4	60	33.6	1.490
5	80	44.8	1.491
6	100	56.1	1.493

The refractive index determination of the different analytes was performed according to ASTM 542 testing standards.

3. SPR theory

Surface plasmon resonance (SPR) phenomenon was initially observed in the early 1900s by Wood. Anomalous narrow dark bands were observed in the diffracted spectrum when a metallic diffraction grating was illuminated by polychromatic light [10]. In the late 1960s, Otto, Kretschmann and Raether gave the theoretical explanation to these anomalies and designed experiments to excite surface plasmons [11]-[13].

Comprehensive reviews of theory and experimental approaches regarding the plasmonic resonance phenomenon are reported in literature [10]-[21].

A surface plasmon, by definition, is a quantum of a surface charge density oscillation. Surface plasmon waves are charge density oscillations propagating along a metal - dielectric interface. Under certain conditions, the electromagnetic incident wave resonantly couples from a free space wave to a surface-plasmon wave resulting in phenomenon of surface-plasmon resonance.

3.1. Excitation of surface plasmons

Recently J. Homola *et al.* [14] as well as S. Kawata *et al.* [15] gave a comprehensive review on most widely used applications of SPR based sensor types.

A common application of exciting surface plasmons is realized by making use of the prism-coupled approach, which was initially demonstrated by Kretschmann, Raether and Otto. Exciting surface plasmons in this context is based on attenuated total internal reflection [11],[13].

Investigations conducted in this work focused on the approach of surface plasmon excitation on basis of the Kretschmann configuration due to its simplicity, robustness and flexibility to adapt to specific applications.

In this setup, incident beam photons, through a prism, is reflected toward a detector (see next section for more details). When the wavevector of the incident beam photons matches the wavevector of SPR conditions, incident beam photons resonantly couple with electrons in the metal layer. Resonating electrons penetrate the metal and propagate as surface plasmons on the opposite side of the layer.

Shaping the incident beam wavevector to match SPR conditions is achieved by either changing incident beam properties or the angle of incidence. At a certain incident angle, known as the resonance angle, SPR conditions are evident in an intensity loss of the reflected beam, which appears as a dip in the SPR reflectivity curve.

The surface plasma wave is a TM-polarized wave (magnetic vector perpendicular to the direction of propagation of the SPW and parallel to the plane of the interface), whose wave vector k_{sp} propagating at the interface between metal and dielectric can be expressed as [22],[23]:

$$k_{sp} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} \tag{2}$$

where ε_m is the permittivity referred to the metallic film and ε_d is referred to the dielectric.

At visible wavelengths, this condition is fulfilled by several metals of which gold and silver are the most commonly used [24].

The incident angle allowing to match the SPR conditions can be calculated as:

$$\theta_{resonance} = sin^{-1}\left[\frac{\sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}}}{n_{prism}}\right] \tag{3}$$

Eq. (3) demonstrates the wave vector dependence of the coupling structure properties and the permittivity of the investigated medium ε_d.

A typical SPR reflectivity curve is shown in Fig. 1, which relates the reflected incident beam intensity to the angle of incidence.

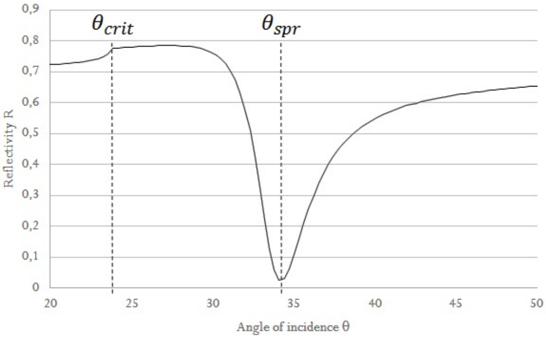

Fig. 1. Typical angular interrogation result of an SPR experiment

The response of the sensing system is characterized by two specific events of the reflectivity curve: a) a rise in the reflected beam intensity is observed up to reach the critical angle, θ_{crit}, which is defined by the optical properties of the prism; b) a significant dip in the SPR reflectivity curve at a higher incident angle, which is referred to as the SPR angle. At this particular angle, the incident beam wavevector matches SPR conditions and it is evident in an intensity loss of the reflected beam.

4. Numerical simulations

The SPR transducers have been simulated by means of Winspall, according to the representation of Fig. 2.

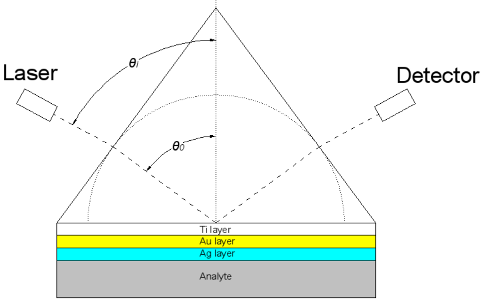

Fig. 2. Schematic order of metallic films deposition on the optic prism

In this work, 704 different configurations have been simulated, changing the parameters summarized in Table 2. All simulations have been performed, ranging the incidence angle θ_i between 0° and 90°.

Table 2. Cases under numerical simulation

Parameter	Value
Laser wavelength [nm]	460, 530, 665,860
Prism material	BK7, BAF10, LASF9, SF10
Thickness of Ti layer [nm]	0, 2
Thickness of Ag layer [nm]	15, 20, 25, 30
Thickness of Au layer [nm]	15, 20, 25, 30

The layer of Ti, if present, is in contact with the prism to guarantee optical continuity between the prism and the metal films. Particularly, the sequence of the layers is: glass prism, Ti layer, Au and/or Ag layers, analyte.

Finally, in the last part of this paper, as post-processing of results, in order to choose the best configuration of the SPR sensing device (single or multilayer, material and thickness), a numerical analysis has been carried out to identify the configurations with the higher sensitivity. The sensitivity (*S*) of a sensor is defined as the change in the monitored parameter *Y* (in this work resonance angle and reflectance) with respect to the parameter *X* to be determined (refractive index) [25].

$$S_\theta = \delta\theta_{SPR}/\delta n \qquad (4)$$

$$S_R = \delta R/\delta n \qquad (5)$$

Where S_θ is the resonance angle sensitivity and S_R is the reflectance sensitivity.

S_θ indicates how much the resonance angle position varies with respect to the refractive index at the metal/dielectric interface: a greater slope of sensitivity curve indicates that the sensor has a greater ability to detect small change in the refractive index of the sample, while S_R indicates the change in reflectance that is observed at a fixed angle of measurements.

Taking into account that a sensor with fixed laser source/detector is simpler to be realized with respect to the moving one, in the present work, the sensitivity parameter S_R has been analyzed, considering the maximum percentage change in reflectance that is observed in the investigated refractive index range. Particularly, each sensor configuration (combination of laser wavelength, optical prism material, metal films and thickness, according to Table 2) has been simulated by changing the refractive index from 1.486 to 1.493 with a step of 0.001.

5. Discussion of results

In this work, numerical simulations have been carried out in order to find the best solutions in terms of sensitivity. Particularly, the numerical results allowed to define several optimal configurations of SPR sensors, one for each kind of sensing layer (only Au, only Ag, Ti-Au, Ti-Ag, Ti-Au-Ag). Table 3 summarizes the main parameters of the best cases under investigation.

Table 3. Best solutions for each kind of layer

Number of case	Layer	Laser wavelength	Prism material	Thickness of Ti layer (nm)	Thickness of Ag layer (nm)	Thickness of Au layer (nm)	Angle of maximum sensitivity	Sensitivity
112	Ag	860	SF10		60		78.34	121.88
210	Au	860	BAF10			60	86.78	87.56
309	Ti-Ag	860	BK7	2	30		40.95	0.22
421	Ti-Au	860	BK7	2		30	41.36	0.22
649	Ti-Ag-Au	860	BK7	2	15	25	40.95	0.21

As it is possible to observe, all triangular prisms under investigation admit the best solution with an infrared laser of 860 nm. Furthermore, the single-layer sensors present values of sensitivity much greater than multi-layers ones. For this reason, the Ag and Au based sensors have to be preferred to the others, in order to realize a SPR sensor. The reflectivity curves of the best solution are shown in Figure 3.

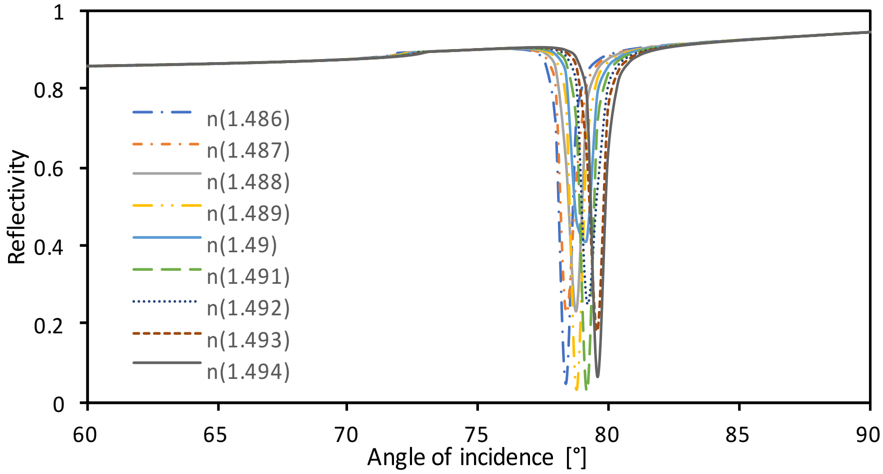

Figure 3. Numerical results: case 860-SF10-AG60

To investigate in depth this result, Figure 4 shows the best sensitivity values of sensors based on Ag and Au films as a function of the incidence angle.

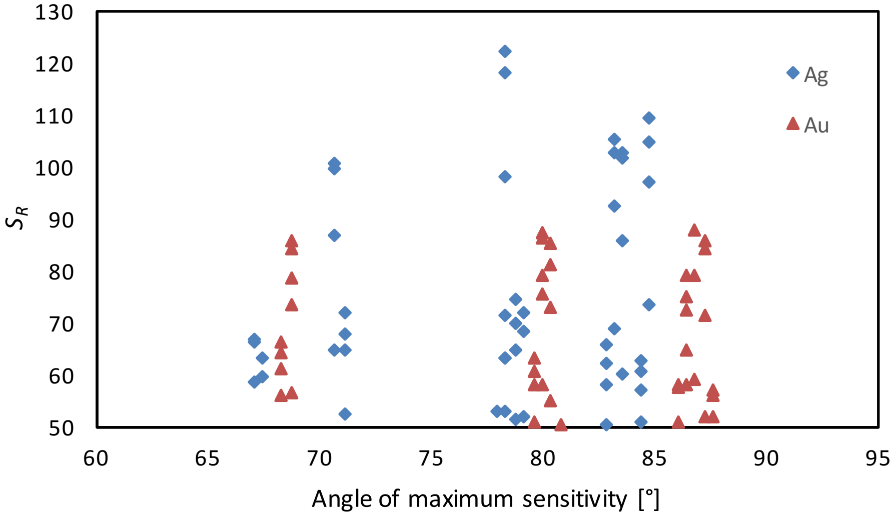

Figure 4. Best sensitivity values of sensors based on Ag and Au films as a function of the incidence angle of maximum sensitivity.

Although the best solution in terms of sensitivity has been obtained by means of an Ag sensor, based on a SF10 prism, at an incidence angle of 78.34° (Table 3), alternative configurations, characterized by high sensitivity, are available at different angles, avoiding for example, optical problems related to high incidence angle.

These data are important under the point of view of industrial applications and in order to establish which sensors can be realized without rotating detector, reducing their production cost.

6. Conclusions

Large two stroke marine diesel engines suffer high Sulphur content within fuels, due to formation of sulphuric acid as a product of reaction of exhaust gases. Therefore, specially blended lubricants with a high $CaCO_3$ concentration are used to prevent sulphuric acid corrosion. At the state of the art, feed rate of lubricant, which is strictly related to neutralization reactions, is established following a function of engine load and sulphur content of fuel oil, but regardless the real formation/neutralization of sulphuric acid within combustion chamber. As a result, its value can be excessive with respect to the stoichiometric quantity, or conversely it could not be enough to complete neutralization reactions.

Taking into account that concentration of $CaCO_3$ within lube oil is related to its refractive index, a useful solution to measure in real time its value can be represented by the SPR sensors.

In this scenario, in this work a numerical optimization of SPR sensor for lube oil characterization has been carried out. Particularly 704 cases have been investigated, changing laser source, optical prism and thickness of 3 metal layers. Mathematical results allowed to find the best sensor in terms of sensitivity. Besides further solutions have been studied in order to evaluate the relationship between incidence angle of laser source and sensitivity.

Acknowledgements

This work was carried out within the project "Analisi e Studi per lo sviluppo di applicazioni tecnologiche basate sulla Risonanza Plasmonica di Superficie (SPR) utili per il controllo di lubrificanti" funded by Ingegnia Srl.

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