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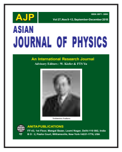

Laser light scattering from rough glass liquid interface: a case study of screening of adulterated diesel oils

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Dedicated to Prof T Asakura

Light scattering is an important phenomenon in various technological applications. For the case of rough glass-liquid interface, it depends on the surface roughness and refractive index mismatch which leads to speckle pattern in the far field region, as well as wetting and variation in the local contact angle. The objective of this work was to study laser light scattering from both rough and smooth glass-liquid interfaces. This was accomplished using a modified handheld gloss meter (portable sensor) which enables recording of time-dependent backscattered laser light (TDBLL) through a software on an integrated laptop. As a feasibility study, authentic and adulterated diesel oils were considered. It is shown that, even though nonzero excess refractive index exists when diesel oils are mixed with kerosene, it has minor role in the dynamic process of liquid spreading. The spreading of liquid as well as excess refractive index depends on the intermolecular interactions which emerges in the measured signals. The different adulterated samples were ordered according to the increase in the volume of the adulterant (kerosene). Hence, the measured TDBLL signals for smooth and rough glass enables distinction between authentic and adulterated diesel oil samples.

Keywords: Light scattering, Refractive index, Backscattered laser light (TDBLL), Kerosene oil

1 Introduction

Professor Toshimitsu Asakura is one of the famous pioneers in the field of laser speckle pattern research of random and partly organized media. His seminal book chapter on speckle pattern from rough surfaces [1] has stimulated scientists to investigate surface roughness properties, such as metals. His work stimulated also us to use speckle pattern from rough glass surface by rather unconventional way namely to screen adulterated diesel oils over a rough glass surface. Using a diffractive optical element for spatial filtering of dynamic scattered light field from spreading fuel drop, we were able to observe hysteresis in the measured scattering signal and the hysteresis was observed for both smooth and rough glass surfaces. The dynamic signal can be used to screen different adulterated diesel oils, and hence such a technique complements for instance, the excess optical properties that we have recently introduced for screening of fake diesel oils [2, 3].

In the present study, the key idea is that wetting depends on the local contact angle between the liquid and glass surface. For rough surfaces, both surface roughness and the local contact angle affect the wetting process, this in turn affects the light scattering. Moreover, for rough surfaces, the contact angle is a local property, which is a subject of hysteresis. The role of surface roughness on contact angle has been a topic of continuous research [4-6]. The theory of contact angle of transparent insulators is rather complicated, and it depends both on the surface roughness and the refractive index of both the insulator and the liquid, and it requires rather wide spectral data for its estimation [6].

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In this case study, the backscattering of laser light is applied to assess its feasibility for separating diesel oils adulterated by different volume fractions of kerosene which is the problematic case of diesel oil adulteration. In our previous studies, we have demonstrated several approaches for the identification of low concentration of kerosene in diesel oil or for the screening of adulterated diesel oils. Firstly, we studied the excess permittivity of binary mixtures of diesel oils and kerosene and it was shown, that while using an Abbe refractometer only or a spectrophotometer only, one may not be able to have enough confidence on the possible suspect of a diesel oil adulterated by kerosene. However, a combination of both refractive index and NIR measurement, and exploitation of so-called excess permittivity of the binary mixture is a useful measure to have a more comprehensive picture on adulterated diesel oils [2]. Secondly, we developed a prototype of an optical liquid sensor for screening of diesel oil adulteration. The prototype is based on a refined sensor that was originally developed for gloss inspection from rough surfaces in field measurement conditions, such as cold-rolling products in metal industry [7]. Such a glossmeter was modified by implementing a removable sensor head that was used in laboratory conditions for the detection of authentic and adulterated diesel oils [8].

The sensor utilized in [8] is the backbone of this work. However, unlike in [8] where the measured signal is the average value of 1000 data points here, all the 1000 data points are recorded through a software on a laptop with wireless integration to the sensor. This functionality enables monitoring of the time-dependent backscattered laser light (TDBLL) signal from glass-liquid interface, which is possible due to hysteresis in the local contact angle especially that of a rough surface. For a dynamic system such as in this study, the contact angle varies with the spreading or wetting of the surface. Therefore, having liquids with different compositions such as authentic and different adulterated diesel oils on top of rough glass, leads to variations in the wetting and spreading process, which consequently leads to different TDBLL signals, and enables us to detect and separate authentic from adulterated diesel oils. Moreover, this method enables identification of heterogeneities and abnormalities that happen when diesel oils are mixed with kerosene, such heterogeneities can sometimes be difficult to spot by looking only at the refractive index values.

2 Materials and methods

The diesel oil sample of this study presents the grades of cold countries (such as Finland), namely summer grade (sample A) whose crude oil is from Russia, and kerosene sample of this study is a low odor commercial product, Alfa Aesar brand (sample B). The binary mixtures of these samples were prepared by blending diesel oils with kerosene in the proportions of 5%, 10% and 15%. The refractive index for each of the authentic fuel samples together with their mixtures, was measured at room temperature with the aid of Abbe refractometer (Atago RX5000) operating at wavelength of 589 nm with relatively high accuracy of ±0.00004. The NIR transmittance spectra of the samples were measured at room temperature with a spectrophotometer (Perkin Elmer Lambda 9) and a quartz cuvette. This device measures transmittance in UV-VIS-NIR range with an accuracy of 0.07% transmittance for absorbance value equal to 1. However, in this study, our interest was to get the spectral properties of the fuels at 635 nm, because it is the wavelength of operation of the portable sensor utilized in this work.

The laser light source and detector are incorporated in a single commercial device (handheld glossmeter (MGM-Devices, Finland)) [7] whose sensor head was modified to enable operation with rough as well as smooth glass containing fuel drop. The sensor head is a glass slide (VWR microscope slide ECN 631 – 1150) with refractive index of 1.4570 at 635 nm, with diameter and thickness of 25 mm and 3 mm, respectively. To compare our results, we performed the experiments on two similar glass slides whereby a drop of 50 μL volume of the various liquids was introduced with a pipette on the glass surface. One of the slides has one of its surfaces roughened with diamond grinding pads and the measured average roughness, Ra = 0.48 µm, was determined with the stylus profilometer. The surface grinding results in a Gaussian height distribution function [9].

The portable device is incorporated with a diffractive optical element (DOE) which spatially filters the speckle field from the specular reflections from an object or a surface and passes the resulting intensity onto a single-cell photodiode detector.

The incident light source is a low-power (0.8 mW) semiconductor laser, lasing at 635 nm which is comparable with the average surface roughness of the glass. The angle of incidence and detection are at 6 degrees to the normal. The beam is focused to 50 µm at the 2 mm aperture in contact with the glass slide containing the liquid drop. Moreover, the portable device provides a wireless integration to a laptop via an infrared (IR) transmission. With the aid of a laptop, it is possible to measure and record the 1000 data points using the software on the laptop instead of just one average signal reading provided on the display of the device. Therefore, through this integration (Portable device and laptop) it is possible to monitor the time-dependent backscattered laser light (TDBLL) signal from the glass-liquid interface. When different liquids are introduced on either the rough or smooth surface the properties of the glass-fuel interface change, likewise refractive index matching or mismatching also occur leading to different intensities of TDBLL signal which consequently enables identification of fake from authentic diesel oils.

3 Results and discussion

The refractive indices of the fuel samples measured by the Abbe refractometer at 589 nm are shown in Table 1. It is obvious that the refractive index of authentic diesel oil is the highest followed by adulterated samples in the order of increasing adulteration percentage, while kerosene has the lowest refractive index value. A more detailed analysis of refractive index readings for sample A is given in [2], where it was shown that, chemical interactions occur when diesel oils are mixed with kerosene. Furthermore, the absolute refractive index values for the fuel samples of this study at 635 nm are also presented in (Table 1), these were calculated by applying the singly subtractive Kramers-Kronig relation (SSKK) on spectrophotometric data which utilize the anchor point data at 589 nm. The theoretical formulations of SSKK as well as its application to obtain the spectral data away from the anchor point are demonstrated in [2]. The refractive index data for authentic diesel oil and kerosene at 635 nm were utilized to calculate the ideal refractive index for the adulterated samples from the equation:

$$n_{\text{ideal}} = \sqrt{(f\, n_{\text{DO}}^2 + (1-f)\, n_{\text{KE}}^2\,)} \tag{1}$$

where n_{ideal} is the ideal refractive index, n_{DO} is the refractive index of authentic diesel oil, n_{KE} is the refractive index of kerosene, and f is the volume fill fraction of authentic diesel oils. The excess refractive index, which is a measure of chemical activity was obtained as follows:

$$n_{\text{excess}} = n - n_{\text{ideal}}, \tag{2}$$

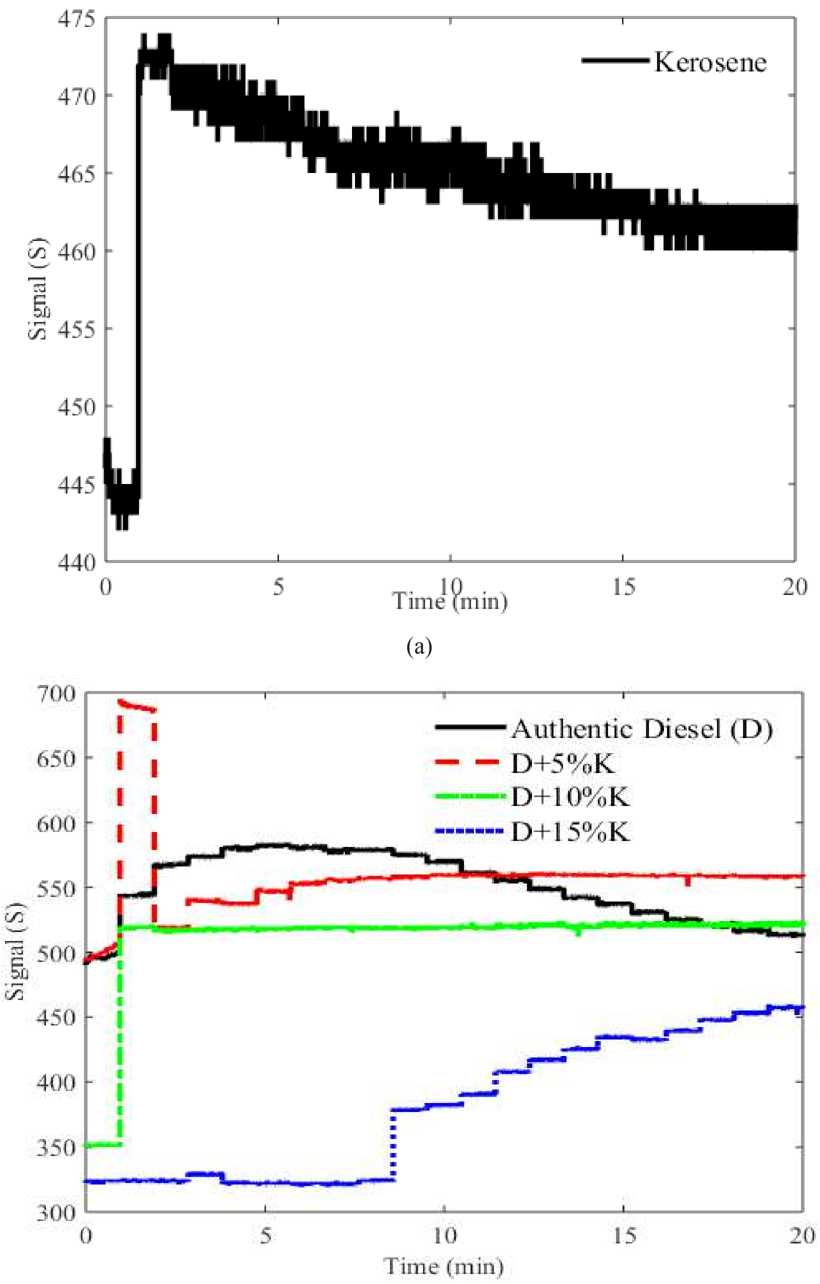
where n is the refractive index obtained from SSKK analysis. The obtained excess refractive index data at 635 nm are also presented in (Table 1). It is obvious from (Table 1) that there is moderate excess refractive index for adulterated samples, and the excess refractive index for both 5% and 10% samples have the same value while that of 15% has a higher value, hence showing molecular interactions between different hydrocarbons.

Figure 1 shows the TDBLL signal for the different fuel drops spreading on the smooth glass. In [8] we studied the use of backscattering signal (S) from a portable prototype optical sensor at two-time instances, 1min and 20 mins. However, in this work, we instead monitor the time dependency of the signal for a period of 20 mins at the 1-min intervaland exploit it in the screening of diesel oil. The steps in Figures 1 and 2 correspond to the time lag in measurements (1-min) where there is accumulated hysteresis in the contact angle. This is predominant in the case of the kerosene on the rough surface (Fig 2(a)) which could be due to its high wettability, especially, at initial interaction with the surface. The detected backscattered signal is the convolution of refractive index mismatch between glass and fuel, reflections from the glass surface, and multiple reflections between boundaries. Figure 1(a) shows the behavior of kerosene on smooth glass surface, it is obvious from (Fig 1(a)) that there is sharp rise in the beginning followed by monotonic decrease as the time advances. On the other hand, in Fig 1(b) are shown the TDBLL signals for authentic and adulterated diesel oils, it is obvious from (Fig 1(b)) that authentic diesel oil shows slow but continuous increase in the signal at the beginning followed by monotonic decrease as time advances. For the case of adulterated diesel oils interesting phenomenon is observed, namely the curves of adulterated diesel oils are located below the authentic diesel oil and the curves are located lower and lower as the percentage of kerosene increases. However, there is an interesting feature with 10% as compared to 5% and 15%, namely a plateau type time signal. Thus, this system experiences less hysteresis than the other adulterated samples. The explanation could be based on the intermolecular interaction of the different hydrocarbon molecules that balance the hysteresis and leads to a rather stable spreading regarding rather the constant value of TDBLL. In the realm of light interaction, the smooth surface exhibits a more regular spreading of a liquid drop, and the signal from smooth surface depicts the changing surface curvature without contributions from surface scattering. The abnormal behavior cannot be seen in the excess refractive index but there exists intermolecular interactions for this particular sample despite showing less hysteresis and fluctuations in comparison with 5 and 15% samples.

Table 1. Refractive indices of the fuel samples measured with the table Abbe refractometer at 589 nm, absolute refractive index obtained using SSKK at 635 nm, and ideal refractive index at 635 nm.

Sample	Volume percentage of kerosene	Refractive index at 589 nm	Absolute refractive index at 635 nm	Excess refractive index at 635 nm
A	0%	1.46373	1.46371	
	5%	1.46269	1.46266	0.00002
	10%	1.46163	1.46160	0.00002
	15%	1.46060	1.46057	0.00006
B		1.44230	1.44226	

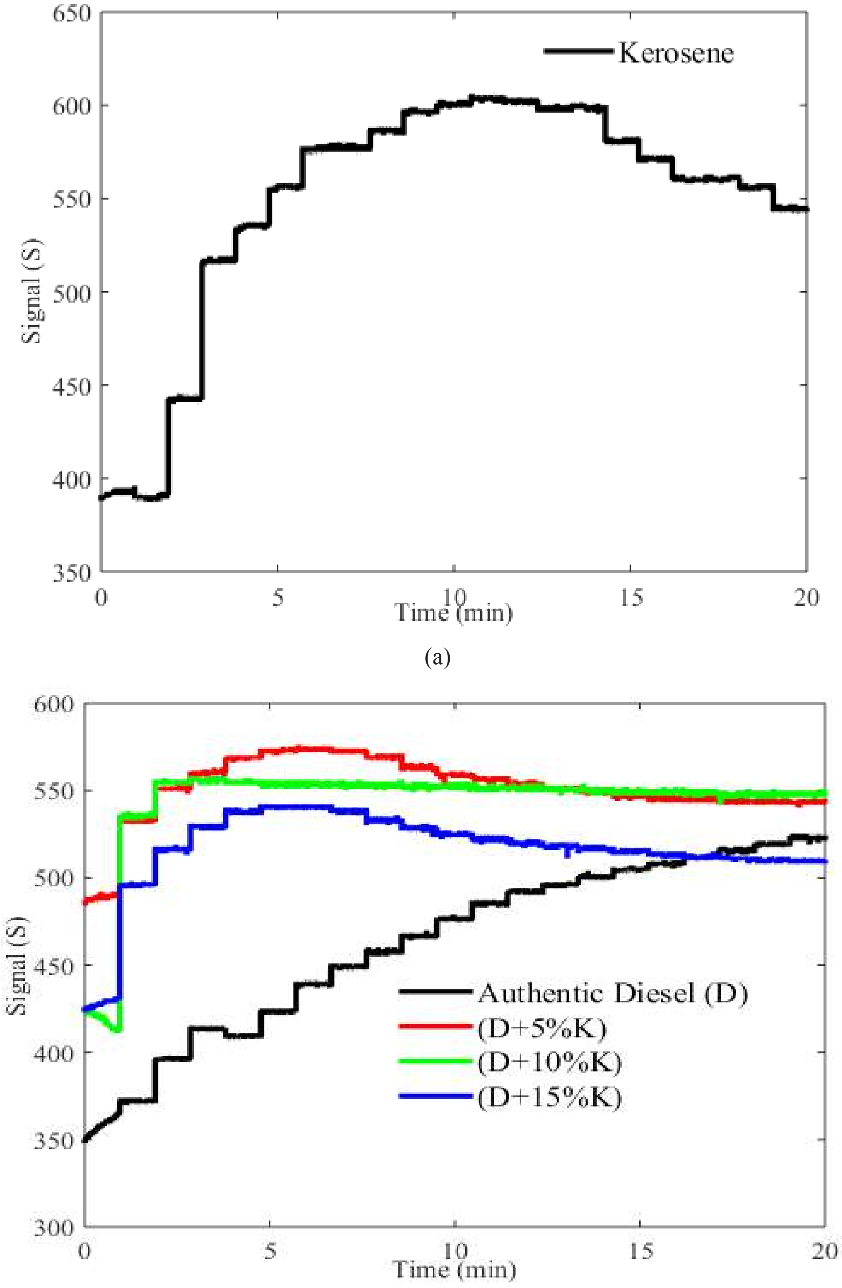
Figure 2(a) shows the TDBLL signal for kerosene drop spreading on the rough glass, and that of the authentic and adulterated diesel oils on the rough glass surface. It is obvious from (Fig 2(a)) that unlike the case of smooth glass, there is a gradual rise, with more apparent hysteresis, to a maximum signal value and subsequent decrease in the signal as time advances. From (Fig 2(b)), it is obvious that there is a slow but continuous increase in the signal as the time advances for the case of authentic sample. In the case of adulterated diesel oils, we observe that the TDBLL signals of the adulterated samples are higher than that of the authentic sample. Usually, according to conventional binary mixing rules, the signal for the adulterated sample is expected to be in between that of the authentic diesel oil and kerosene. This indicates that the binary mixing rules are violated in this case. However, as the volume of kerosene increases, the signal strength approaches that of authentic diesel oil. This is completely the opposite of what was observed in (Fig 1(b)). Surprisingly, the 10% adulterated sample shows pretty much similar time signal behavior for the rough surface compared with that of the smooth surface -the TDBLL signal plateaus. Comparing the signals from both surfaces, it appears that the rough surface has little influence on the spreading of the 10% adulterated sample resulting in the similar signal behaviour. This is again probably due to the intermolecular interactions, which necessarily may not affect the excess optical property (i.e. refractive index) but affects the wetting.



(a)

(b)

Fig 1. The time dependent back scattered laser light (signal (S)) from the fuel-smooth glass surface. (a) for kerosene, (b) for pure and adulterated diesel oils. The steps correspond to the time lag in measurements caused by hysteresis.



(a)

(b)

Fig 2. The time dependent back scattered laser light (signal (S)) from the fuel-rough glass surface. (a) for kerosene, (b) for pure and adulterated diesel oils. The steps correspond to the time lag in measurements caused by hysteresis.

From Figs 1 and 2, we observe non-smooth curves which suggest the presence of hysteresis in the spreading of a liquiddrop on both the rough and smooth surfaces.. On smooth surfaces, pure liquid with lower contact angle is expected to easily spread than on rough surfaces. On the contrary, spreading of liquids on rough surfaces are characterized by the “stick-slip” flow. This is in agreement with previous studies where hysteresis was demonstrated [10, 11]. Anyhow, we can conclude that the liquids, both genuine and fake diesel, behave differently on the two surfaces with distinguishable features in the TDBLL signal, allowing us to be able to screen the adulterated from the authentic diesel oil.

It is obvious that the excess refractive index had little role in the dynamic process of liquid spreading. However, both spreading and excess refractive index depend on intermolecular interactions of different hydrocarbons present in the mixtures of diesel oil and kerosene. These interactions are obviously seen in the non-zero excess refractive index and emerging also in the measured signal.

The measured TDBLL signal on both smooth and rough surfaces shows a rather calm signal which is linear in the larger part of the considered time interval for the case of 10%. However, if we consider the excess refractive index values for all adulterated samples in (Table 1) it is obvious that, these are not zero and there is no drastic value for 10% which could explain its strange behavior in TDBLL signal as compared to 5% and 15%. Moreover, the excess refractive index values are same for both 5% and 10%. Therefore, optical properties explain the behavior of the samples only partly, showing the existence of intermolecular interactions, which affect the local contact angle. Nevertheless, the behavior of 10% cannot be explained purely based on the optical properties, the excess refractive index is necessary but not sufficient factor. Yet all three adulterated samples have completely different time dependent signals and can be screened and identified based on the differences in their TDBLL signals.

4 Conclusion

In this work, we have studied the scattering of laser light from rough glass-liquid interface by using a modified handheld gloss meter (portable sensor) in laboratory conditions. This was achieved by measuring the time-dependent back scattered laser light (TDBLL). The measured signal is dictated by the refractive index mismatch between the glass and liquid, as well as liquid drop spreading on the glass including contact angle and hysteresis.

The behavior of both authentic and adulterated diesel oils on rough and smooth glass surfaces were the focus of this feasibility study. It is herein demonstrated that nonzero excess refractive index exists when diesel oils are mixed with kerosene. However, it has a little role in the dynamic process of liquid spreading but makes it difficult to differentiate the samples based only on the refractive index measurements. The spreading of liquid as well as excess refractive index depends on the intermolecular interactions which emerge in the measured signal. The measured TDBLL signal enables distinction between authentic and adulterated samples. Moreover, in the measured TDBLL signal for both rough and smooth glass the different adulterated samples are ordered according to the increase in adulteration level. We propose this method to be applied for screening of fake diesel oils.

References

1. Asakura T, in *Surface roughness measurement*, (ed) Erf K, (Academic Press. INC, New York) 1978, pp 11-49.
2. Kanyathare B, Peiponen K-E, *Appl Opt*, 57(2018)2997-3002.
3. Kanyathare B, Peiponen K-E, *Sensors*, 18(2018)1551; doi.org/10.3390/s18051551
4. David R, Neumann A W, *Langmuir*, 29(2013)4551-4558.
5. Wolansky G, Marmur A, *Langmuir*, 14(1998)5292-5297.
6. Rosenholm J B, Peiponen K-E, Gornov E, *Adv Colloid Interface Sci*, 141(2008)48-65.
7. Kuivalainen K, Oksman A, Juuti M, Myller K, Peiponen K-E, *Opt Rev*, 17(2010)248-251.
8. Kanyathare B, Kuivalainen K, Räty J, Silfsten P, Bawuah P, Peiponen K.-E, *JEOS:RP*,14(2018)1-6.
9. Tanner L H, *Opt Laser Technol*, 8(1976)11-116.

10. Rahimi P, Ward C A, *Microgravity Sci Technol*, 16(2005)231-235.
11. Marmur A, *J Colloid Interface Sci*, 168(1994)40-46.

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