It is the weight, not numbers of experiments that is to be regarded.

- Isaac Newton

Chapter 4

Integrated Optic Sensor for detecting adulteration in petroleum based products
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4.1 Introduction

In the recent years although extended research on the effects of fuel properties been performed worldwide, but we find that adulteration of petroleum product especially petrol, kerosene and diesel (high speed diesel (HSD)), has become a serious problem. Skyrocketing prices of petroleum product is the only worry that the consumers are facing with the issue of purity. Even after paying a good price for them, the rampant practise of adulteration of petroleum product has overwhelmed the market. Further, it is seen that the metropolitan growth is too associated with rising number of automobiles to meet chiefly public conveyance and goods transport. Adulteration differs from contamination in that; people deliberately add cheaper products like kerosene [1]-[2] to pure petroleum products like petrol or diesel in an endeavor to lift profit margins. This in turn lowers the octane number [3] of the fuel. The price differential in the market of various petroleum products is the main driving force for this malpractice of adulteration and hence, it motivates for the illegal mixing of a cheaper fuel with a more expensive fuel. [4] [5]. The adulteration of petrol by diesel and that of diesel by kerosene is difficult to detect [6]-[12]. Further, it has been found that mixing kerosene with diesel does not lead to an increase in tailpipe emission, but contributes to air pollution indirectly. All engines are designed and manufactured to run on specified fuel. They emit substantially more pollutants if the fuel specification is changed and poorly maintained. Often, but not always the adulterated fuel lessen the life of engine components and also reduces performance of the engine. And as a result, these practices lead to losses in several areas, which include some damaging of the engines and deterioration in air quality through increased emissions. In the recent years we find that, due to the high demand and good price of petrol, it is very much prone to adulteration.

As described in chapter-3, the designed optical sensor with the embedded planar
waveguide geometry was developed using the Silicon Oxynitride (SiON)/SiO$_2$ waveguide technology and has been adapted for detecting adulterated petroleum products such as petrol, kerosene and diesel. This chapter discusses in detail an adulteration detection technique, using evanescent wave sensing principle.

4.2 Design of the waveguide sensor for adulteration applications

We consider a waveguide structure as depicted in Fig. 4.1, consisting of a guiding (core) layer of Silicon Oxynitride (SiON) [Refractive Index (R.I), $n_c=1.46$], deposited on silica-on-silicon substrate and sensing region of refractive index, $n_s$ as a cladding and an outside medium (air) with refractive index $n_a$ that is less than R.I of core. The dispersion equation of waveguide sensor structure is derived in chapter 3 as:

$$
\alpha_x = m \pi + \cot^{-1} \left( \frac{\cosh \alpha_x + \frac{\gamma(C)}{\alpha_x} \sinh \alpha_x}{\alpha_x \left( \frac{1}{\gamma(C)} - \frac{1}{\alpha_x^2} \sinh \alpha_x \right)} \right) \tag{4.1}
$$

where $\gamma(C) = \sqrt{\beta^2 - k_0^2 n_s^2(C)} \tag{4.2}$

and $n_s(C)$ is the refractive index of sensing region depending on concentration (C) of the adulterant.

Fig-4.1: 3D view of the planar optical waveguide sensor with sensing region placed on the top of silica on silicon substrate.
The most important quantity when speaking about optical sensing is the power flow inside the different layer of the optical waveguide. The sensitivity of the sensor is dependent on the fraction of total power propagating inside the core of the waveguide. From the dispersion relation, given by Eq. (4.1) as discussed in detail in section 3.2.1 of chapter 3, the following expression for the estimation of normalized power along the z-axis of waveguide core is obtained as:

\[ W(z) = W'(0)e^{-\frac{\alpha z}{\delta(C)}} \]  

where \[ W'(0) = \left( \frac{0.0018}{n_s(C) - 1.3315} \right) W(0) \], \[ W(0) = \frac{k^2 \pi^2}{\Gamma(C)} \],

\[ \Gamma(C) = \frac{4\alpha^2 \gamma^2 e^{-2\gamma t(x_2-x_1)}}{\beta^2 \delta(C)^4 \alpha_2 g (1 + \gamma x_1)} \], \[ \delta(C) = \sqrt{\alpha^2 + \gamma(C)^2} ; \]

\[ \alpha_g = \sqrt{k_0^2 n_c^2 - \beta^2} \], \[ \gamma_g = \sqrt{\beta^2 - k_0^2 n_c^2(C)} \], \[ \beta_g = \sqrt{k_0^2 n_c^2 - \alpha^2} \]

Fig-4.2: Normalized power versus length of the waveguide along z-direction for different \((x_2-x_1)\) ~ 375 \(\mu m\), 475 \(\mu m\) and 575 \(\mu m\) with \(n_{sub}=1.45\) and \(n_c=1.46\) respectively.
Fig. 4.2 shows the normalized power $W(z)/W(0)$ versus $z$ of the waveguide along the $z$-direction for different thicknesses of the cladding layer $(x_2-x_1)=375 \, \mu m$, 475 \, \mu m and 575 \, \mu m$ respectively. From the figure it is seen that $W(z)/W(0)$ decreases with increase of $z$ and this variation saturates at $z=90,000 \, \mu m$ for the mentioned $(x_2-x_1)$ values. For $z<90,000 \, \mu m$ the rate of decrease of $W(z)/W(0)$ for $x_2-x_1=475 \, \mu m$ was found to be more than that for $x_2-x_1=375 \, \mu m$ but for $x_2-x_1=475 \, \mu m$, it is close to that for $x_2-x_1=575 \, \mu m$. So, we have chosen $x_2-x_1=475 \, \mu m$ and length of waveguide as 90,000 \, \mu m.

4.2.1 Sensitivity response

The sensitivity of the sensor is dependent on the fraction of total power propagating inside the core of the waveguide. From the dispersion relation given by Eq. (4.1), the waveguide sensitivity $S_w$ (i.e. the rate of change of effective refractive index $N$ with respect to refractive index $n_s$ of the sensing medium) is obtained as:

$$S_w = \frac{\delta (\beta/k_o)}{\delta n_s(C)}$$  \hspace{1cm} (4.4)

where $\beta$ is the propagation constant, $k_o = \frac{2\pi}{\lambda}$, $n_s(C)$ is the refractive index of sensing region depending on concentration (C) of the adulterant. The sensitivity of the proposed planar waveguide sensor is then analyzed for detection of adulteration in petroleum product. For detecting such petroleum adulteration, adulterated petroleum product was used as a sensing material which acted as the cladding layer of the planar waveguide sensor and was put inside the cylindrical enclosure (CE).

Fig. 4.3 shows the sensitivity of the waveguide sensor versus core refractive index $(n_c=1.45)$ with $x_2-x_1=475 \, \mu m$ for different core width ($2x_1$) of the waveguide. It is observed that sensitivity increases slightly with increase of $n_c$ and independent of waveguide core thickness. This is because the sensing area does not increase with increase of $n_c$ and $x_1$. 
4.2.2 Limit of Detection (LOD)

In the proposed waveguide sensor for adulteration detection, we find that the signal at the output of the sensor is independent of refractive index of the sensing region for \( n_s \geq n_c \), as the signal will no longer be confined in the core region. So, the limit of detection (LOD) of our sensor will be restricted up to core refractive index and for our experimental setup as shown in Fig. 4.4, Limit of Detection (LOD) is, 1.333-1.46.

4.2.3 Estimation of sample volume

The sample volume of the sensor was set at 0.25 ml. This is calculated using the relation,

\[
\text{Sample Volume} = \text{Inside Volume of } PCE - \text{Volume of Waveguide Sensor} \quad (4.5)
\]

where, volume of waveguide sensor = volume of waveguide core and volume for wafer and lower cladding on silicon substrate.

Thus,

\[
\text{Sample Volume} = \pi r_{PCE}^2 L_{PCE} - W_{PCE}^2 L_{PCE} - \text{W}_{\text{substrate width}} \times L_{\text{substrate}} \times T_{\text{substrate}} = 0.25 \text{ ml}
\]

where \( T_{\text{substrate}} = 310 \mu m \); \( L_{\text{substrate}} = L_{\text{PCE}} = 90,000 \mu m \); \( W_{\text{substrate width}} = 1000 \mu m \), and

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Fig-4.3: Waveguide sensitivity versus \( n_c \) of the proposed waveguide structure with different core width (2\( x_1 \)).
rpCE = 1000 μm; W = core area = 50 μm respectively.

4.2.4 Estimation of detection time

The total detection time of the sensor is obtained, using the relation:

\[ T_{tot} = T_{refill} + T_{response} \]

and \( T_{response} \) = detector response time \( \sim 800 \) ps [13] which is very small in comparison to \( T_{refill} \). And so, detection time \( (\tau_D) = T_{refill} \) and is obtained as:

\[ Detection \ Time \ (\tau_D) = \frac{\pi rpCE^2 L_{PCE}}{v} \]

\[ = \frac{0.25}{1} \text{ml/mlsec}^{-1} \]

\[ = 0.25 \text{sec} \]

(4.6)

where \( v \) = flow rate of sample \( \sim 1 \) ml/sec, \( rpCE \) is the radius of the cylindrical enclosure and \( L_{PCE} \) is the length of the cylindrical enclosure that holds the planar waveguide sensor inside. We have seen in experimental set up that beyond this value of detection time, the experimental set up is unstable. Detection time is the sum of filling up time of sample and response time. The response time is 800 ps which is very small in comparison to filling up time of sample.

4.2.5 Material and methods

4.2.5.1 Procurement of petroleum product samples

Pure petrol, diesel and kerosene were procured from Indian Oil Corporation (IOC), Assam Oil Division (AOD), Digboi, Assam, India.

4.2.5.2 Preparation of samples

The adulteration for these samples has been made using the relation:

\[ Concentration \ of \ diesel = \frac{x}{x+y} \times 100\% \]

(4.7)

where \( x \) = volume of diesel and \( y \) = volume of petrol.
4.2.5.3 Design parameters

Table 4.1 shows the design parameters used for the proposed planar waveguide optical sensor.

<table>
<thead>
<tr>
<th>Design parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of the sensor (L)</td>
<td>90000 μm</td>
</tr>
<tr>
<td>Width of the sensor</td>
<td>1000 μm</td>
</tr>
<tr>
<td>Refractive index of core ((n_e))</td>
<td>1.46</td>
</tr>
<tr>
<td>Length of substrate ((L_{substrate}))</td>
<td>90000 μm</td>
</tr>
<tr>
<td>Radius of PCE ((r_{PCE}))</td>
<td>1000 μm</td>
</tr>
<tr>
<td>Core area ((W))</td>
<td>50 μm</td>
</tr>
<tr>
<td>Sensing area width ((x_2-x_1))</td>
<td>475 μm</td>
</tr>
<tr>
<td>Lower cladding</td>
<td>310 μm</td>
</tr>
<tr>
<td>LOD</td>
<td>1.333-1.46</td>
</tr>
<tr>
<td>Sample volume</td>
<td>0.25 ml</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>4.1</td>
</tr>
<tr>
<td>Detection time</td>
<td>0.25 secs</td>
</tr>
</tbody>
</table>

4.3 Experimental results and Discussion

As discussed earlier in section-3.4.1 of chapter-3, the waveguide sensor structure was fabricated on thermally oxidized <100> Si wafers. The embedded SiON waveguide core of width~50 μm was deposited by plasma enhanced chemical vapour deposition (PECVD) and the refractive index was tailored by controlling different gas concentrations (SiH₄, N₂O and NH₃). The waveguide patterns are transferred by standard photolithography, developed and etched by Reactive Ion Etching (RIE) using CF₄ and O₂. The designed and fabricated waveguide sensor using SiON technology with core refractive index 1.46 was housed within a cylindrical enclosure (CE) as shown in Fig. 4.4, with efficient butt couplings between the input fiber to waveguide sensor and waveguide to output coupling fiber to reduce the fiber/waveguide coupling losses during our experimental work.
Fig-4.4: Photograph of the experimental set up for adulteration detection using planar waveguide optical sensor

Fig-4.5: Block diagram of the experimental set up for use of the planar waveguide based sensor for adulteration detection.

In the experiment, He-Ne laser of wavelength 632.8 nm is taken as the light source. At first for validating its waveguide characteristics, we have measured the normalized power using distilled (DI) water as reference solution with the designed sensor placed inside the cylindrical enclosure (CE). Then the variation of the detected power with
change of adulterant concentration in petrol, kerosene and diesel has been measured using an optical power meter. The normalized powers $W(z)/W(0)$ for detecting the adulteration have been measured using the experimental set up as shown in Fig. 4.5, where $W(0)$ is measured with distilled water in the sensing region.

![Photograph of the Abbe Refractometer (Model: CAR-02 Make: Contech) for Refractive Index Measurement](image)

Even if there are minute variations, the variations in the normalized output power with adulteration would pursue an analogous trend. Since the sensor operates with reference to a reference sample, so by appropriately choosing the right reference adulteration is determined as the variation in the normalized output power would be due to adulteration only.

All experiments were conducted at room temperature $23^\circ$C. The effect of temperature has also to be ascertained to make the sensor to be useful in practice. The variation of the refractive indices with adulterant (for petrol, diesel and kerosene) has also been measured by using an Abbe refractometer (as shown in Fig. 4.6). The refractive indices of petrol, kerosene and diesel as measured using an Abbe refractometer (Model: CAR-02 Make: Contech) are found to be 1.419, 1.436 and 1.461 respectively. It is very much mandatory to find whether there are variations in the refractive indices of petrol, kerosene and diesel after adulterating.
Fig. 4.7 shows the variation of refractive index (RI) versus concentration of kerosene mixed with pure petrol. It is found that the RI value increases with increasing concentration of adulterant (here kerosene is used as the adulterant). Whereas, in Fig. 4.8 we see that there is a decreasing trend of RI variation with increasing concentration of kerosene mixed with diesel. Fig. 4.9 shows the variation of RI versus increasing concentration of kerosene for both petrol and diesel.

![Refraction Index Graph](image)

**Fig-4.7:** Refractive index versus kerosene concentration.
Fig-4.8: Refractive index versus kerosene concentration.

Fig-4.9: Refractive index versus kerosene concentration.
Fig. 4.10(a) shows the measured normalized power $W(z)/W(0)$ versus measured diesel concentration for petrol with diesel, where $W(0)$ is the incident power coupled to the sensor using experimental set up (as shown in Fig. 4.4). It is seen that the normalized power decreases with increase of diesel concentration. This is due to the fact that the refractive index (measured by Abbe refractometer) increases with increase of diesel concentration (as shown in the inset of the figure) as the number of light rays confined in waveguide sensor decreases. The similar type of behaviour is obtained in the case of $W(z)/W(0)$ versus concentration of kerosene for kerosene mixed with petrol. The rate of decrease of $W(z)/W(0)$ in case of kerosene mixed with petrol is slightly more than that in case of diesel mixed with petrol.

![Normalized power versus diesel concentration](image)

**Fig-4.10(a):** Normalized power versus diesel concentration.

We have also studied $W(z)/w(0)$ versus diesel concentration for diesel mixed with petrol as shown in Fig. 4.10 (c). It is seen that the rate of decrease of $W(z)/W(0)$ with respect to diesel concentration is slightly more than those for petrol with kerosene and petrol with diesel.
Fig-4.10(b): Normalized power versus kerosene concentration

Fig-4.10 (c): Normalized power versus diesel concentration
Fig. 4.10(d): Normalized power versus kerosene concentration for petrol+diesel (5%), petrol+diesel (10%) and petrol+diesel (20%) respectively. It is seen that the measured normalized power decreases with the increase in kerosene (used as the adulterant).

4.4 Performance comparison
Table 4.2 shows the comparison of the performance of our experimental set up with other existing experimental set ups of sensor. It is seen that in our proposed optical waveguide sensor the sample volume required for testing of adulteration of petroleum products is 0.25 ml which is 160 times less than that required for fiber optic sensor, reported by S. Roy [12]. Further, we find that the waveguide sensitivity of our planar waveguide sensor is 4.1 which is quite higher in comparison to other works because of having large sensing region of our proposed sensor. The limit of detection (LOD) of our waveguide sensor is 1.33-1.46 which is higher than the previous work [4]. Finally, it is seen that the detection time of this proposed waveguide based optical sensor is ~ 0.25.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity</td>
<td>0.14 NM/ %</td>
<td>-</td>
<td>4.1</td>
</tr>
<tr>
<td>LOD</td>
<td>3.57 x 10^-4 RI</td>
<td>-</td>
<td>1.333-1.46</td>
</tr>
<tr>
<td>Sample volume</td>
<td>-</td>
<td>80 ml</td>
<td>0.25 ml</td>
</tr>
<tr>
<td>Detection time</td>
<td>-</td>
<td>-</td>
<td>0.25 secs</td>
</tr>
</tbody>
</table>

### 4.5 Conclusion

In this chapter, an optical waveguide sensor of length 90,000 μm and core width ~50 μm incorporating composite planar waveguide geometry (as described in Chapter-3) have been adapted for rapid detection of adulterant traces in pure petroleum products such as petrol, kerosene and diesel. The sensor sensitivity has been analyzed for detecting the adulterant traces in pure petroleum products, procured from Indian Oil Corporation Limited (IOCL), Assam Oil Division (AOD) Digboi, Assam. We find that the sensitivity of the sensor is dependent on the fraction of total power propagating inside the core of the waveguide. The waveguide sensitivity is obtained as ~4.1 which is ~40 times more than that of the existing planar waveguide sensors [14] and ~20 times more than that of asymmetric waveguide structure [15]. The technique allows spot determination of adulteration in pure petroleum products without involving the use of chemicals. Further, this approach preserves the miniature dimensions of the sensor and simplifies the instrumental design requiring only very minimal sample volume for its sensing purpose. Advantages include high sensitivity, easy fabrication and more importantly, requirement of very minimal sample volume for detecting adulteration.

### 4.6 List of References


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