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Determination of Adulteration in Diesel by Refractive Index Measurements

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Abstract:

The diesel sample is many times adulterated with low-boiling solvents like Naptha or kerosene. Determination of adulterants in Diesel, Kerosene and Petrol is a great challenge to police, revenue and forensic department. The literature methods are time-consuming and tedious with scope for errors. The refractive index measurement of known admixtures of diesel and kerosene at 27^{o}C gives a linear plot. The Refractive index comparisons of the unknown sample with known admixtures directly give the percentage of kerosene in diesel. Diesel in kerosene admixtures in the ratios 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20 and 90:10 were prepared. Known admixture and unknown sample's refractive index were measured at 27^{o}C. The Refractive index was measured twice for accurate measurements. The intercept of the refractive index of the unknown sample on a straight line graph of known admixture directly gives the percentage of kerosene in diesel. Kerosene is used to adulterate diesel. This approach was used to detect adulterated diesel samples referred to forensic science laboratories.

Keywords: Forensic, Diesel, Refractive index

Introduction

In several countries, fuel adulteration is very common, this is because the products of comparable quantities have different prices. Adulteration in petroleum products is a great menace to the Nation. Petroleum products like diesel (HSD) petrol (motor spirit), etc. are widely adulterated due to their high prices, heavy demand, and supply scarcity. The purity of high-priced fuels is governed by IS1460 [1]. Diesel is the most widely used fuel in heavy vehicles and is often adulterated with cheaply available domestic kerosene fuel. Kerosene (calorific value 45 KJ/g) is made available at a subsidized rate to the economic class as cooking fuel and industrial fuel by the Indian government. But blackmailers mix this kerosene with diesel. The mixing of kerosene with diesel plays havoc in automobile machines resulting in damage to internal engine spares and causes decreasing the fuel efficiency of the machine. The overlapping properties of kerosene and diesel attracted the illegal mixing of kerosene in high-priced diesel for monetary gains. Diesel fuels are petroleum-derived complex mixtures of hydrocarbons C9-C19 with a calorific value of 45 KJ/g, a distillation range is approximately 140-400^{o}C and do not contain any olefins. Diesel in India contains 15-30% aromatics and 70-85 % saturated aliphatic. Aromatics present are polynuclear rings and a very small concentration of individual hydrocarbons. On the other hand, saturated aliphatics contain a considerable amount of individual hydrocarbons [2-4]. Government authorities like Police Civil Supply Departments monitor the quality of diesel and petrol from dealers through a random collection of samples. Forensic and other authorized laboratories receive samples from police or civil supply departments. In laboratories, samples were analyzed based on ISI specifications using physical parameters which are quite inaccurate and defective. Adulterated diesel samples with 30% kerosene get passed based on these specifications. There is no 100% accurate and efficient method or technique in the literature for qualitative adulterant estimation of diesel. The ISI specifications have no meaning unless the percentage of adulteration is specified in the sample. In the recent past, several workers claim new accurate methods for the quantification of diesel and also received good responses. These methods included the determination of physical parameters like distillation range, specific gravity, opacity measurement of intrinsic modulated fibre optical density [5] etc. Theoretical interpretation of certain physical methods involving mathematical calculations is cumbersome and time-consuming [6]. The hydrocarbons in diesel (C9 to C19) and kerosene (C6 to C16) are overlapping and hence have the potential for adulteration. The performance of diesel engines is the function of compression ratio, injection time and the mechanism of fuel resulting in ignition delay occurrence. Analytical instruments like gas chromatography, mass spectrometry, distillation analyzer and flash point etc. help in the measurement of adulterations in diesel [7]. The public distribution (PDS) product is dyed with blue dye, whereas the one used for industrial purposes is colourless.

ISI have a specified density range for kerosene and diesel which are overlapping and hence definite conclusion cannot be drawn. Other methods including flash point determination, are not useful for the determination of adulteration [8]. A gas chromatographic and specific gravity criterion for the rapid study of adulterations in diesel with kerosene is described in the literature [9]. Specific gravity for diesel samples varies from 0.800 to 0.850. The specific gravity of kerosene varies from 0.780 to 0.820 quite overlapping. Online fractionation and identification of polycyclic aromatics in diesel fuel can be done by two-dimensional microbore high-performance liquid chromatography, Capillary gas chromatography [10]. Also, the gas chromatographic method for the determination of adulteration in diesel samples is described [11- 13]. The analysis of diesel was also done by using GC x GC x MS methods [14-17]. Gas chromatography [18, 19], NIR and IR [20] Spectroscopy [21, 22]. And Super Fluid Chromatography [23, 24] etc methods are also used for this purpose. Diesel is a mixture of petroleum fractions and there is a lot of variation in their percentage, therefore it is quite difficult to conclude the adulteration of kerosene in a diesel by gas chromatographic methods. The cetane number method needs an engine, which is expensive and generally not available in laboratories, also the amount of sample required is about 5 litres. This method is not useful for the detection of adulteration in lower percentages. In the present work, an attempt was made to address the problem using the measurement of the refractive index

Experimental

Instrumentation:
Make-Anton Paar
Model No.-RXA170
Detection temperature: 22^{o}C; Acetone (washing solution)

Ten different samples of kerosene and diesel were obtained from different standard sources. Four to five drops of samples were put in the sample cell of the refractive index instrument. The instrument shows valid results and gives the actual values of the refractive index (Table 2).

Table 1. The refractive index of ten different diesel and kerosene samples

Sample No.	Diesel At 27oC	Kerosene at 27oC
1	1.4604	1.4450
2	1.4600	1.4457
3	1.4599	1.4456
4	1.4603	1.4461
5	1.4606	1.4438
6	1.4611	1.4456
7	1.4612	1.4471
8	1.4611	1.4446
9	1.4605	1.4449
10	1.4608	1.4445

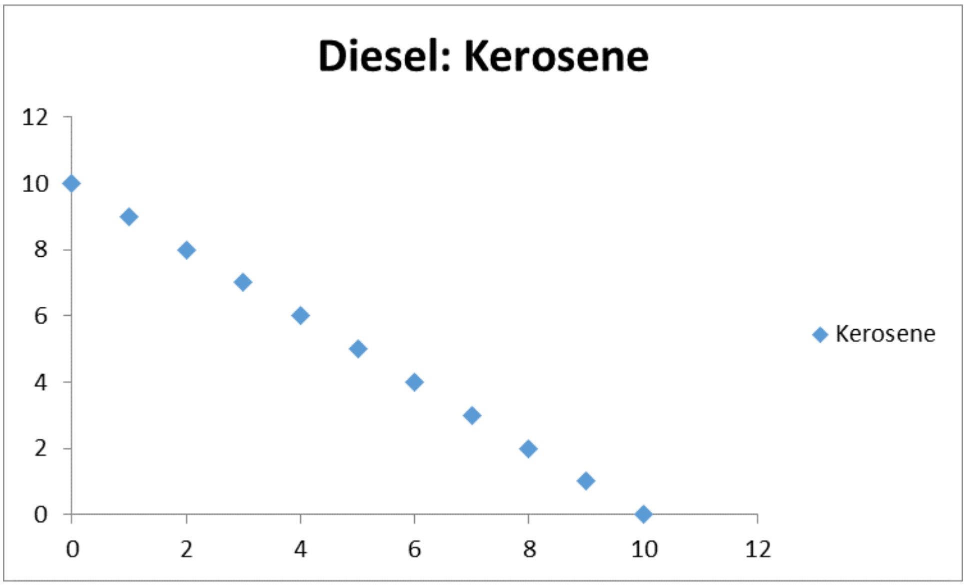
Diesel and kerosene samples were procured from refineries. Admixtures of diesel in kerosene in the ratio (9:1), (8:2), (7:3), (6:4), (5:5), (4:6), (3:7), (2:8) and (1:9) were prepared

Table 2. Refractive index diesel kerosene admixture samples

Diesel	Kerosene	Refractive index at 27^0 C
10	0	1.4604
9	1	1.4587
8	2	1.4571
7	3	1.4556
6	4	1.4540
5	5	1.4523
4	6	1.4507
3	7	1.4491
2	8	1.4477
1	9	1.4461
0	10	1.4444

Results and Discussion

The values of the refractive index of ten different diesel samples range from 1.4600 to 1.4612 (average 1.4606). The values of the refractive index of ten different kerosene samples range from 1.4445 to 1.4471 (average 1.453). as shown in Table 1.
The measurement of the refractive index of admixtures shows that there is a decrease in the refractive index as the percentage of kerosene. The graph of refractive index is linear with an increase in the percentage of kerosene as shown in graph 1.



Graph 1: graph of Diesl: Kerosen admixture

Table 3: Refractive index measurments of suspected adulterated samples

Suspected sample	**Refractive index at 27^0 C**	**Remark**
1	1.4573	Adulterated
2	1.4507	Adulterated
3	1.4587	Adulterated

Conclusion

Measurements of refractive index is simple techniques for the determination of adulteration in diesel by kerosene. With the help of refractive index measurments we can find out adulteration up to 10 percent.

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