Experimental Study on Adulterated Gasoline and Diesel Fuels

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Automotive petro-fuels mean particularly gasoline and diesel which are provided mainly from petroleum industry by refining crude oil. Adulteration of these petro-fuels with low priced materials is wide spread throughout the world in general, and India in particular. This can result in sub-optimal performance of transportation fuels, resulting emissions of toxic pollutants from vehicles. Therefore, the present experimental study is carried out systematically on adulterated gasoline and diesel fuels with kerosene, diesel and used oil respectively. Various tests related to these petro-fuels were carried out and compared with the standard specifications. The results have been discussed qualitatively taking into account the changes in characteristics of these fuels and their impact on engine performance and exhaust emissions.

Keywords : Adulterated petro-fuels; Refining crude oil; Toxic pollutants; Exhaust emissions

INTRODUCTION

The transportation fuels, namely, gasoline and diesel are in maximum use today worldwide. As the number of vehicles has increased five times in ten years from 33.6 million in 1996 to 168.0 millions in 2006, and is still increasing, the demand of these fuels has also increased. The consumption of gasoline and diesel fuel for the last few years[1, 2] is shown in Table 1. Thus, worldwide dependence on petro products have been therefore aiming to maximize the production of petro-fuels by setting up new refineries and expanding the present capacity by adopting newer technologies. In spite of all these efforts, there remains a gap between the supply and demand in India. Due to pronounced rise in import, because of the shortfall in indigenous production, the domestic prices will continue to increase in the forthcoming years. For the benefit of poorer sections of the people, the prices of diesel and kerosene are kept low, but the rogue people take the advantage of these low priced fuels and use them to adulterate with high cost fuels. Such malpractices thus lead to continuous shortage of kerosene and diesel and invariably worsen the environmental problems. Apart from this, there are other possibilities of different fractions to get adulterated at the point of storage and transportation, which may result in problems during use.

Thus, adulteration of petro-fuels namely gasoline and diesel is very common and one of the major causes of excess emissions of toxic pollutants such as smoke, particulate matters, hydrocarbons, SOx and NOx etc[3-11]. The increase in vehicle emission is an unavoidable side effect of the increased mobility of people and greater accessibility of goods and services. Air pollution adversely affects human health through cardiovascular and respiratory systems and is associated with premature mortality as well as sickness. SOx and NOx are the main precursors of acid rain that can harm forests, lakes and river ecosystems. Polluted air is the major cause of global warming. A large number of vehicles has led to diminishing green cover in the city and vehicular pollution has become a serious health issue. The motor spirit and diesel (regulation of supply and distribution and prevention of malpractices order, 1998), defines adulteration as the introduction of a foreign substance into motor spirit/ high speed diesel, illegally with the product that does not confirm to the requirements and specifications of the product. The foreign substances are called adulterants which when introduced alter and degrade the quality of the

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Table 1 Consumption of motor gasoline and diesel in Mt

Product	1993-94	1996-97	2001-02	2006-07
Gasoline	3.75	7.00	9.10	11.57
Diesel	28.70	36.20	40.80	76.68

Table 2 Gasoline specifications in India

Characteristics	BS-II	BS-III	Euro-IV
Year of implementation	2000-2001	2005	2010
Sulphur, ppm	500	150	50
RON, min	88	91	91
MON, min	-	81	81
Benzene, max.,vol%	5/3	1	1
Aromatics, max., vol%	-	42	35
Olefins, max., vol%	-	21	21
RVP, kPa	35-60	60 max	60 max
Density, 15°C, kg/m³	710-770	710-770	
Copper strip corrosion for 3 h at 50°C	Not more than no 1		

Table 3 Diesel specifications in India

Characteristics	BS-II	BS-III	Euro - IV
Year of implementation	2000-2001	2005	2010
Sulphur, ppm	500	350	50
Cetane No.	48	51	51
Density, kg/m^3	820-860	820-845	820-845
95% Recovery, °C	370	360	360
PAH, wt%	-	11	11
Flash point			
• Pensky Martens closed cup	66	66	
Water content,%	0.05	-	
CFPP, max			
• Winter	6°C	6°C	
• Summer	18°C	18°C	
Copper strip corrosion for 3 h at 100°C	Not worse than no 1	Not worse than no 1	

base transport fuels. Thus, there are different types of adulterations[4-11] for these transportation fuels such as

- blending variable amounts of hydrocarbons based industrial solvents into gasoline.
- blending small amounts of distillate fuels such as diesel and kerosene into gasoline.
- blending variable amounts of kerosene into diesel.
- blending small amounts of heavier fuel oils into diesel.

GASOLINE AND DIESEL FUEL ADULTERATION

Adulterating gasoline with kerosene which is more difficult to burn than gasoline, results in higher levels of hydrocarbons, carbon monoxide, and particulate matter emissions. Large amount of kerosene addition may also cause fall in octane quality, resulting in incomplete combustion, toxic emissions and can lead to engine knocking. When gasoline is adulterated with diesel fuels, the same effects occur but usually at lower levels of added diesel. Both diesel and kerosene added to gasoline will increase engine deposits. Gasoline may also be adulterated with gasoline boiling range solvents like toluene, xylene and other aromatics. Larger amounts of toluene and /or mixed xylenes cause some increase in hydrocarbons (HC), CO, NOx emissions, and increase in level of air toxins, especially benzene in the tail-pipe exhaust. The adulterated gasoline itself could have increased potential human toxicity if frequent skin contact is allowed. For gasoline, any adulterant that changes its volatility can affect drivability. High volatility (resulting from addition of light hydrocarbons) in hot weather can cause vapour lock and stalling and low volatility in cold weather can cause starting problems and poor warm up.

The adulteration of diesel with kerosene does not increase emissions but for low sulphur diesel, it could cause the sulphur level to exceed the specification, increasing sulphate based particulate emissions, which are major atmospheric pollutants. Diesel engines mainly emit respirable suspended particulate matter (RSPM) with a particle diameter of less than 10 micron. The addition of heavier fuel oils to diesel is usually easy to detect because the fuel will be darker than normal, resulting some increase in both exhaust particulate matter (PM) and polyaromatic hydrocarbon emissions (PAH).

In literature, there are very few data in this respect[3,11-13], therefore experimental evaluation for each case is very much relevant to make the consumers aware of the adulteration to save the engine life and most important the environment. Therefore, the present work is carried out with an objective to have a systematic evaluation of petro products on the engine performance and on the environment. Indian specification of gasoline and diesel have been summarized in Table 2 and Table 3, respectively[3,8,11,12].

EXPERIMENT

The petro-fuels, namely, gasoline and diesel were procured from local petrol pump, Aligarh. Kerosene was procured from the local market having following properties: smoke point: 23 mm(smoke point apparatus : IP 57/95, make: SUR Berlin), refractive index(RI): 1.44587nD at 19°C (digital refractrometer, make : Kruss optronic.), copper strip corrosion:2c (copper strip corrosion : IP 154, make : SUR Berlin),carbon residue: 0.01 wt.% (Conradson method: ASTM D189-01, make SUR Berlin), water content: 0 vol% (Dean and Stark method : ASTM D 95-99, make : SUR Berlin) and flash point: 50°C (Pensky Martens closed cup method: ASTM D 93-00) and used oil was procured from auto workshop having following properties(refractive index:1.4898, copper strip corrosion : 3c, Conradson carbon residue:0.1278 wt %) .

Standard (ASTM/IP) tests[5] were thereafter accomplished to evaluate the properties of the gasoline and diesel fuels and the adulterated samples of the following five categories. The percentage contribution of pollution load from gasoline and diesel vehicles are presented in Table 4.

- Gasoline +Used oil
- Gasoline + Diesel
- Gasoline + Kerosene
- Diesel + Used oil

Table 4 Percentage contribution of pollution load from gasoline and diesel vehicles

Category of Vehicle	CO	HC	NOx	SO_2	Pb	PM
Petrol	67	84	5	4	100	-
Diesel	33	16	95	96	-	100

- Diesel + Kerosene

In each case, the properties with respect to the major components were tested.

RESULTS AND DISCUSSION

Blends of used Oil in Gasoline

When gasoline is mixed with even small amount of used oil, then a drastic change in gasoline properties are obtained, as shown in Table 5. The various properties like specific gravity (with hydrometer), API gravity, reid vapour pressure test (RVP), copper corrosion, RI values and distillation ranges(as per ASTM D86) are affected drastically. The RVP values change significantly as the blending of used oil in gasoline increases. Thus, it may be inferred that the presence of heavy hydrocarbon in gasoline decreases the RVP values, resulting in starting problems of the engine. The values for copper strip corrosion also changes significantly as the amount of used oil is increased. These values do not meet the Indian specifications for gasoline. Thus, these blends will emit toxic gases from tail pipe emissions and also deteriorate engine parts. Hence, it can be concluded that adulteration by even small amount of used oil in gasoline would adversely affect the environment. The API gravity also changes, indicating the presence of heavier hydrocarbons in gasoline. The RI are obtained with the help of digital refractrometer. RI values are least affected due to addition of used oil in gasoline. From the distillation data as shown in Figure 1, it is observed that change in IBP, FBP and other values is significant. The IBP values increase as the amount of used oil in gasoline increases. The changes are appreciable for 5% and 10% blending of used oil in gasoline, as shown in Figure 1 (T10 and T30). The IBP values are important as it shows front end volatility. However, for 15% blending, the change is unexpected, it is further noted that the increasing change is seen for T90 values to 10% blending and after that it decreases. Similarly, the FBP values increases up to 10% adulteration and then decreases for 15% blend. Residue content also increases as the concentration of used oil in the sample increases. The highest value is observed in the case of 15% blend as per expectation. This would lead to improper combustion and PM will increase in the exhaust emissions.

Table 5 Properties of blends of used oil in gasoline

Properties	Blends (volume of used oil in gasoline %)				
	0 %	2.5 %	5 %	10 %	15 %
Specific gravity (15°C)	0.731	0.742	0.757	0.760	0.780
API gravity (15°C)	62	59	55	53	50
Reid vapour pressure (38°C) bar	0.70	0.640	0.595	0.520	0.490
Copper strip corrosion	1 a	2 A	2 B	2 C	3 B
Moisture content, vol %	0.6	0.6	0.6	0.7	0.7
Refractive Index (n_D), 21°C	1.380	1.430	1.44	1.45	1.45

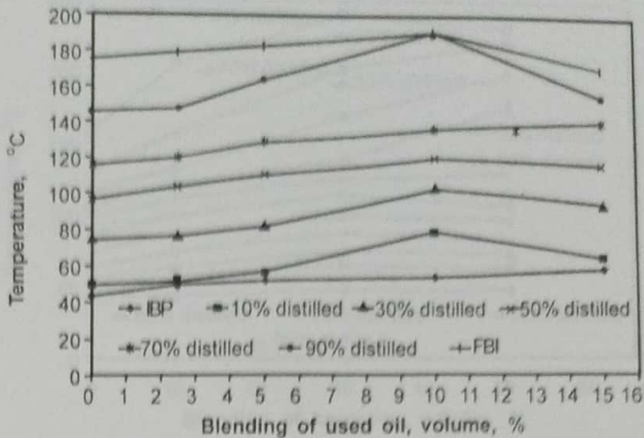

Figure 1 ASTM curves for blends of used oil in gasoline

Blend of Diesel in Gasoline

Table 6 and Figure 2 give the results of adulterated gasoline with diesel. API decreases as the percentage of diesel increases showing the presence of much heavier hydrocarbons. Values of refractive Index also increase as the percentage of diesel increases from 10% to 50%, thus the amount of heavier hydrocarbons and aromatics increases which are harmful to the environment[11]. For gasoline, copper strip corrosion value is not worse than 1a, meeting the Indian specifications. As proportion of diesel increases, the copper strip corrosion value becomes worse and the adulterated sample does not meet the specifications and causes severe corrosion. Due to vast difference between the boiling ranges of the two samples, distillation range is affected most. The value of IBP is only slightly changed from the value of pure gasoline. The maximum variation is seen for 50% diesel adulteration which is around 47%. On adulteration with diesel, RVP value decreases significantly and on 50% adulteration the percentage decrease in RVP value is 61%, showing the presence of large amounts of heavy hydrocarbons.

Table 6 Properties of blends of diesel in gasoline

Samples	Tests			
	API gravity, °API	Refractive index, nD	Copper corrosion	Reid vapour pressure, bar
Pure(100% gasoline+ 0% diesel)	62.335	1.3647	1a	0.457
90% gasoline+ 10% diesel	55.470	1.4347	3b	0.330
70% gasoline+ 30% diesel	51.198	1.4457	3b	0.235
50% gasoline+ 50% diesel	41.758	1.4572	3c	0.180

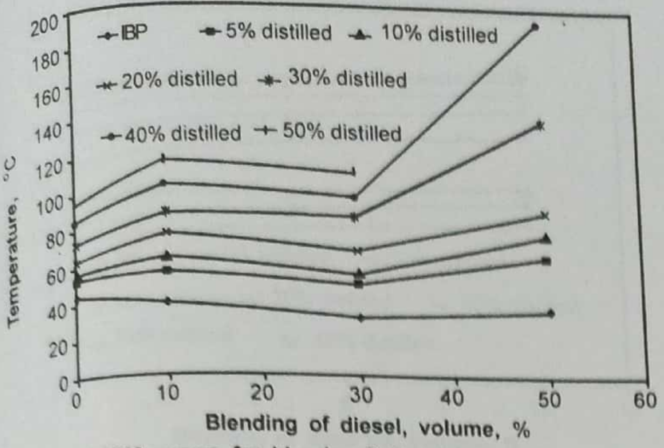

Figure 2 ASTM curves for blends of diesel in gasoline

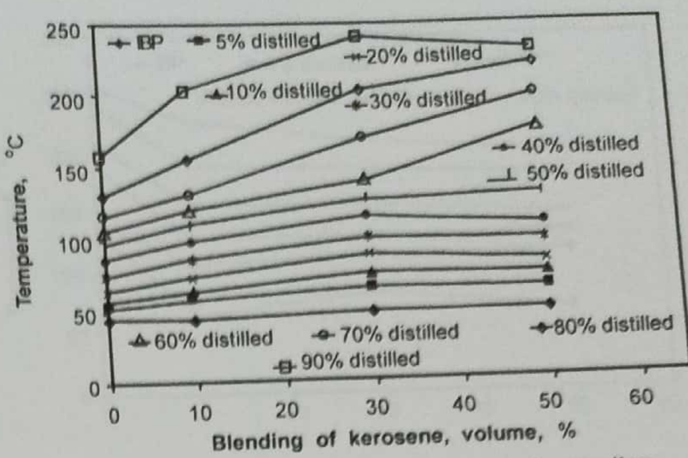

Figure 3 ASTM curves for blends of kerosene in gasoline

Blends of Kerosene in Gasoline

From Table 7, it is clear that the refractive index is the least affected property for 10% and 30% blends of kerosene. However, as the kerosene is increased upto 50%, the RI values increases, showing the presence of heavy hydrocarbons and aromatics in the sample. The RI values determine the purity as well as the presence of aromatic content in the sample. As gasoline is adulterated with kerosene, the value of API decreases, for 10% adulteration it is 59.819, and for 30% and 50% mix, these values are 57.117 and 52.600 respectively, which are also within the permissible limits and reflects that 30% and 50% samples contain large amounts of heavier hydrocarbons. The most affected property for gasoline is RVP which is an important criterion to evaluate the performance of gasoline. For pure sample, this value is 0.457 bar which is within Indian specification. On adulteration with kerosene, RVP decreases significantly. On 50% adulteration the percentage decrease in RVP value is 57 %, showing the presence of large amounts of heavy hydrocarbons. Thus engine performance with respect to volatility is affected to a significant extent. Such an adulteration may affect the cold start, warm up, crankcase oil dilution, engine deposits. Figure 3 shows the ASTM curves for different blends of kerosene in gasoline. Distillation data shows that the change in IBP is marginal for 10% kerosene blending. For 30% mixing, there is a slight change in IBP values. Only T90 value is slightly more than Indian specification values. Thus, back end volatility is related to engine deposits and engine oil dilution. The copper strip corrosion test is also important as it signifies the presence of sulphur content in the sample. If any sample contains large amounts of sulphur, it would enhance corrosion of engine parts and also emit toxic gases like SOx, which can adversely affect the environment. For pure gasoline, this value is within the permissible limit, but as the amount of kerosene increases from 10% to 50%, this value does not meet specifications, indicating higher concentrations of sulphur compounds in the adulterated samples.

Blends of used Oil in Diesel

Table 8 and Figure 4 show the test results of diesel and used oil mix. It can be observed that conradson carbon residue (CCR) values increase to a much large extent and for 7.5% mix this value is 0.1262. The RI values also increase, as diesel is adulterated with used oil, showing the higher concentration of harmful substances that cause environmental pollution. Copper strip corrosion values as well as total sulphur determined by standard tests also indicate greater amounts of presence of sulphur in the adulterated fuel, causing harmful emissions to the environment. Sulphur can cause wear in diesel engine and

Table 7 Properties of blends of kerosene in gasoline

Samples	Tests			
	API gravity, °API	Refractive index, nD	Copper corrosion	Reid vapour pressure, bar
Pure(100% gasoline+ 0% kerosene)	62.335	1.3647	1a	0.457
90% gasoline+ 10% kerosene	59.819	1.4222	2b	0.350
70% gasoline+ 30% kerosene	57.116	1.4265	3b	0.245
50% gasoline+ 50% kerosene	52.600	1.4338	2c	0.196

Table 8 Properties of blends of used oil in diesel

Samples	Tests			
	CCR wt, %	Refractive index, nD	Copper strip corrosion	Sulphur content wt, %
Diesel	0.0011	1.4700	3a	1.2067
97.5% diesel + 2.5% used oil	0.02616	1.4724	3b	1.3678
95% diesel + 5% used oil	0.0674	1.4782	3c	1.4086
92.5% diesel + 7.5% used oil	0.1262	1.4800	3c	1.5081

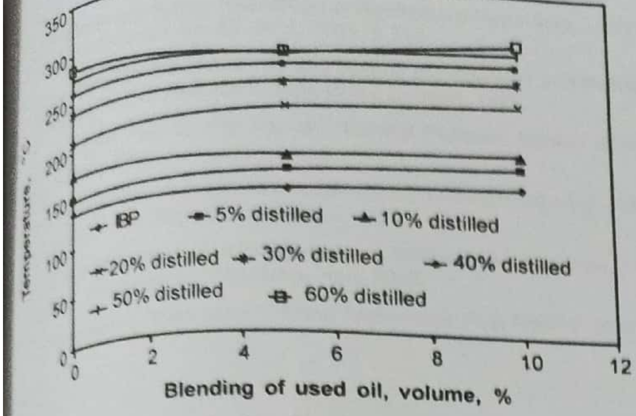

Figure 4 ASTM curves for blends of used oil in diesel

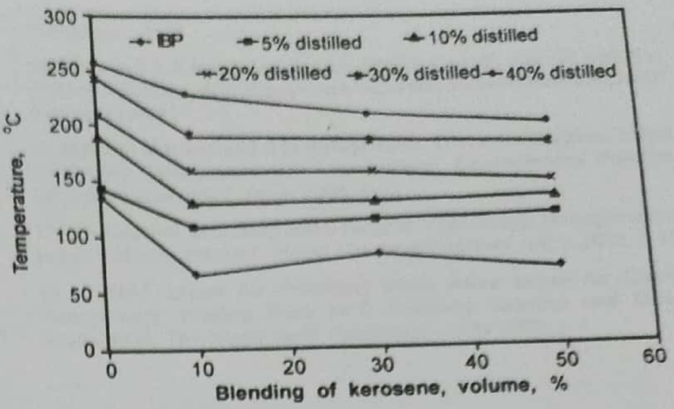

Figure 5 ASTM curves for blends of kerosene in diesel

Table 9 Properties of blends of kerosene in diesel

Samples	Tests						
	API gravity, °API	Refractive, index nD	Copper corrosion	Aniline point, °C	CCR, %	Flash point °C	Sulphur content, wt%
Pure diesel	39.807	1.4700	3a	75.0	0.001	49	1.2067
90% diesel+10% kerosene	39.850	1.4688	3b	73.5	0.001	47	1.1467
70% diesel+30% kerosene	40.415	1.4661	3c	72.0	0.005	46	1.0164
50% diesel+50% kerosene	41.906	1.4650	3c	69.0	0.107	46	1.0967

environmental pollution. The sulphur content in HSD engines is going to be reduced to 0.05%. The motivation behind reducing sulphur level is related to direct reduction of particulate emissions as sulphur compounds present in the fuels contribute heavily to the volume of particulate matter emission[9].

Blends of Kerosene in Diesel

Table 9 and Figure 5 shows the various important test results of diesel and kerosene mixture. From the Table, it can be observed that as the percentage of kerosene increases from 10% to 50%, the API value slightly increases, showing no significant change in hydrocarbon type present in diesel. Copper strip corrosion values increases as percentage of kerosene increases, but to a less extent. Aniline point which is a very important property of diesel fuel, decreases as the proportion of kerosene increases indicating the presence of higher amounts of aromatics in the adulterated fuel. Sulphur content for pure diesel can also be determined and it is beyond the permissible limit, and for 50% mixture this value decreases as reported. It is observed that sulphur content decreases as percentage of kerosene increases, showing less amounts of harmful/toxic SOx emissions on combustion of such adulterated fuels. From distillation data, as shown in Figure 5, the IBP values decrease for 10% adulteration, then increases for 30% and become equal to the value for 10% adulteration.

CONCLUSION

The present study gives an idea about the effect of adulteration on the properties of two major automotive petro-fuels in use today. Adulteration of gasoline with kerosene and diesel at higher concentrations can cause serious problems to the engine performance. The adulteration of gasoline with even small amount of used oil would significantly affect the properties of gasoline. Adulteration of diesel with kerosene in higher concentration can cause serious problems of undesirable emissions. Also, adulteration of diesel with even small amount of used oil significantly affects the fuel properties of diesel and cause increased engine deposits and increased harmful emissions. The users can, therefore, avoid the use of adulterated fuels particularly in their vehicles which may cause damage to engine parts.

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