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Case Study

DETECTION OF WATER IN ETHANOL BLENDED PETROL-A CASE STUDY

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A R T I C L E I N F O

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A B S T R A C T

Ethanol blended petrol has come up as an alternative fuel in recent years due to some environmental aspects. As ethanol is hygroscopic, moisture is trapped in underground stored ethanol blended petrol tank and phase separation occurs. Such petrol is not suitable for internal combustion engine. Petrol sample in similar context was received in FSL. After phase separation, each layer was analyzed separately. The present case study successfully shows the composition of alcohol and water in the petrol sample using correlation of different parameters such as density, distillation range, refractive index and gas chromatography.

INTRODUCTION

Adulteration of petrol is very common on petrol pump in our country. Adulteration of kerosene to the petrol leads to the change in properties such as increase in density, change in colour, and change in % recovery of sample. Adulteration of petrol with kerosene are identified, studied and explained by different techniques such as TLC, HPTLC, and GC methods1-7. Generally petrol is stored in underground tank so the mixing of water in petrol is possible. In the last decades, there has been a growing concern with regard to some important environmental aspects. With respect to that view, alcohols are the most popular additives where they have replaced all other additives as octane boosters in gasoline fuel [1-10].

Literature study on the bending of ethanol indicated the addition of 5% ethyl alcohol to petrol does not influence the properties of petrol greatly.[11] Gasohol is gasoline or petrol blended with anhydrous ethanol at different percentages expressed by an E-number, which corresponds to the percentage in volume of alcohol present in the fuel [12]. For instance, E20 contains ethanol at 20% and gasoline at 80%, by volume. The physical properties of up to 20 percent ethanol blends do not differ markedly from petrol. Ethanol blends have a number of advantages over straight petrol including a higher antiknock value, lower exhaust emissions, higher efficiency and possibly more kilometers. Ethanol having hygroscopic properties mix with water in petrol tank. Thus when ethanol in ethanol-petrol blend comes contact with water, will absorb the water, which, if enough is present, will overwhelm the ethanol's ability to remain blended with the gasoline.

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The product is no longer a homogeneous blend of ethanol and petrol, but two layers of product--a layer of gasoline on top and an ethanol layer on the bottom are formed referred to as "phase separation." Phase separation can be a problem for vehicles' fuel lines and ignition system. Many researchers studied the effects of alcohol gasoline blends e.g., ethanol gasoline blends and methanol gasoline blends, on the regulated exhaust emissions of spark-ignition engine. [13, 14]. Turner *et al*[15] studied the effect of ethanol methanol gasoline blends on NOx and CO2 emissions. However, the presence of alcohols in fuel causes corrosion to metallic fuel system components. Elfasakhany[16] discusses performance and exhaust emissions from spark-ignition engine fueled with ethanol-methanol-gasoline blends. Thus many researchers have studied the effects of ethanol blended petrol on ICE.

The case of two phase liquid sample seized from petrol pump in similar context has received in FSL and analysed using different parameters. Purity of petrol in upper layer and percent composition of water and ethanol in lower layer has been studied and results are discussed here**.**

Experimental

Density of the sample was examined using hydrometer. A 100 ml measuring cylinder was properly rinsed with a small amount of the sample, washed and blown dry then filled with the sample to be analyzed. A hydrometer with calibration from 0.70 to 0.80 was submerged into samples and reading was taken at the point of observation of the floating hydrometer. A thermometer submerged into the measuring cylinder was used to stir samples and its reading noted to obtain the temperature of the samples. Determination of distillation range was performed on AutoDist distillation unit. Hanon automatic refractometer was used to find Refractive Index (R.I). All the experiments were carried out at 26^oC

Thin layer chromatography- Thin Layer Chromatography (TLC) technique was adapted to ascertain the presence of orange dye in petrol. Standard Petrol, kerosene(PDS) and orange coloured sample in upper layer was extracted in solvent N-N Dimethyl formamide (DMF) separately and concentrated DMF extract was spotted on TLC Silica Gel (60F 254) plate. The TLC plate was developed in solvent system, Hexane: Acetone (8:2) and spots were observed visually as well as under UV chamber.

Determination of petroleum hydrocarbons by gas chromatography (GC) analysis- The GC System - Nucon model 5765 attached to Nuchrom software was used Operating conditions were; Column: SE 30% packed column, 30 m, 0.25 µm film thicknesses. Carrier gas: Nitrogen 40 ml / min; Detector: FID; Oven Temp: Initial 40^0 C (hold time 2 min), @5^{0}C/min to 100^{o}C hold for 2 min then @10^{o}C/min final temp. 220^{0}C (hold time 5 min); Injector temp-200^{0}C; Detector temp-220^{0}C

For GC, 1 ml standard petrol and sample from upper layer was dissolved in 10 ml ether and 1µl ether extract was used for analysis. Sample in lower layer was also extracted in ether and ether extract of the lower layer was in used for analysis.

RESULTS AND DISCUSSION

Two phases of sample were separated using separating funnel. Both layers were filtered and tested for different parameters as follows:

Primary characterization - Results of the primary characterization of the sample are presented in **table 1**. The upper layer was orange colored liquid while lower layer was colorless. The flammability test for the liquids in both layers was positive. Similarly, the smell of upper layer was of petrol and that of lower layer was mixed hydrocarbons like. On the basis of smell, colour, the upper layer was found to contain petrol. Similarly on the basis of smell, flammability test, copper sulphate test and acidified dichromate test the lower layer was found to contain alcohol along with water.

Table 1 Primary characterization of sample

Sr. No.	Parameters	Upper layer	Lower layer
1	Volume	527 ml	188 ml
2	Colour	Orange colour	colourless
3	Smell	Petrol like	Hydrocarbon like
4	Flammabilty	Highly flammable	Highly flammable
5	Refractive index	1.412	1.373
6	Anhydrous $CuSO_4$	No reaction	Turns blue
7	Acidified Potassium Dichromate	No reaction	Greenish blue colour
8	Schieff reagent	No reaction	No reaction

Determination of physical properties of two phases

Density – Density of pure petrol sample varies in the range of 0.712-0.775 (Laboratory Procedure Manual, 2005)[17]. Density of pure ethanol is 0.789 at 20^{0}C. Density of upper orange coloured layer was **0.**74. Orange colored dye was found on TLC plate matches with the orange coloured dye derived from pure petrol sample and blue coloured spot was not developed for it. The observations confirm presence of petrol in upper layer of sample.

Density of lower layer was 0.856 and the primary characterization of lower layer give clear idea that the lower layer does not contain only water but shows presence of some solvent having density lower than water.

Determination of Distillation range

Distillation range of upper layer sample and lower layer sample with reference to the pure petrol sample has been given in table-

Upper layer

Low density upper layer petrol sample show appreciable similar linear increase in temperature with the percent recovery of the sample as in case of standard petrol sample. Sample in the upper layer follows the same trend as in case of pure petrol. The difference in the results of Final Boiling Point (FBP) do not vary considerably.

Lower layer

The Initial Boiling Point (IBP) of the sample was 73^{0}C. On careful observation the progress of the distillation was slow and considerably stable at 78^{0}C in the range of 15 % to 30% recovery - then 79^0 C in the range of 40%-70% recovery. Slight rise in temperature was observed from 80% - 95% recovery (80^{0}C to 98^{0}C) and then final boiling point was found to be constant (103^{0}C) from 95% recovery respectively. The results of the determination of the distillation range of the lower layer also confirmed the presence azeotropic mixture of ethanol and water.

Table 2 Distillation range profile of sample with reference to standard petrol

% recovery	Reference petrol	Upper layer	Lower layer
0	47.87	46.43	76.54
5	55.32	52.2	77.08
10	57.9	54.57	77.67
15	59.87	56.76	78.06
20	62.25	58.84	78.26
30	66.5	64.68	78.76
40	77.35	80.96	79.06
50	104.1	102.79	79.45
60	117.73	113.08	79.84
70	130.32	119.43	80.62
80	146.12	148.6	82.11
85	156.58	153.23	85.93
90	203.12	180.22	98.87
95	203.29	189.42	103
FBP	204.64	197.45	103.25

Determination of petroleum hydrocarbons

The detection of petroleum hydrocarbons was performed by GC. Chromatogram in Fig 1 indicate that almost all constituents of petrol are present in upper layer of the sample while ether extract of lower layer did not show even the traces of petroleum hydrocarbons.

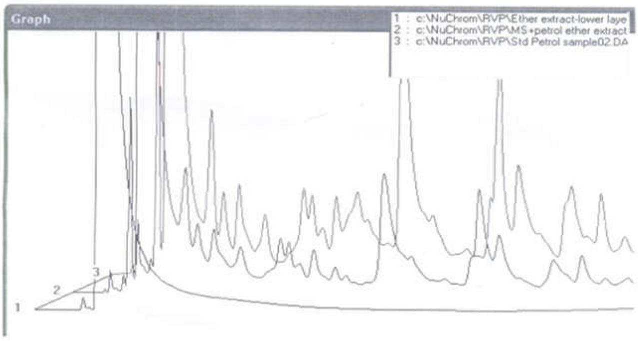

Figure 1 Overlay of ether extract of lower layer (ethanol and water sample), ether extract of upper layer (petrol), and standard petrol sample

Quantification of ethanol and water in lower layer

The presence of ethanol and water in lower phase was confirmed as given in above sections. A mixture of ethanol and water was taken in varying proportion and their densities were determined. The relation of the ratio and the densities of corresponding mixture are given in a figure. The figure clearly indicates corresponding lowering in density of system with increase in percent ethanol.

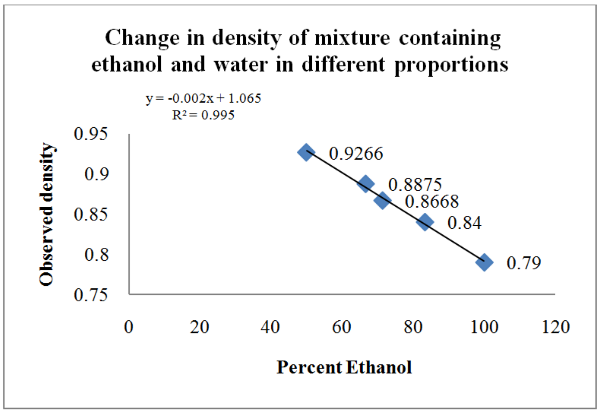

Fig 2 Change in density of mixture containing ethanol and water in different proportions

The density of lower layer was found to be 0.856, this indicate that the given sample may contain about 20% water in the system and over 80% ethanol. The observation found in the distillation study of lower phase also supports the results, wherein the boiling point reaches to 103^0C over about 80% recovery. The present pattern of distillation range in lower layer indicates presence of about 15-20% water and 85-90% ethanol.

CONCLUSION

The results based on density distillation range and TLC clearly indicated the upper layer is unadulterated petrol. On the basis of study of density, distillation range, GC analysis and experimental observations, the lower layer of sample was found to contain about 20% water and 80 % ethanol. A complete separation of ethanol from ethanol blended petrol was found even in the presence of 5% water in the received sample.

In addition to determination of adulteration of petroleum hydrocarbon, the determination of ratio of percent alcohol in water and petrol is the future challenge in forensic investigations. The present study of analysis of two phases gives clear idea about ethanol and water percent in given sample.

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