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Der Chemica Sinica, 2013, 4(3):170-175

Pelagia Research Library
ISSN: 0976-8505
CODEN (USA) CSHIA5

Determination of kerosene in gasoline using fractional distillation technique

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ABSTRACT

The adulteration of petroleum products especially gasoline is a serious problem in many countries. The large differences in prices of gasoline, diesel and kerosene in Jordan are the main driving factor for adulteration. The fact that kerosene is miscible in gasoline makes adulteration an easy task. The unhealthy and unethical practice of adulteration of gasoline with cheaper kerosene or with diesel leads to severely damaging consequences on automotives engines and increases vehicles emissions which are of a major concern to environmental. All engines are designed and manufactured to run on specific fuel, they will emit substantially more pollutants if the fuel specification is changed. When kerosene is added to various types of automotive gasoline, the octane quality will fall below the octane requirements of engine and therefore engine knocking can occur. It is evident in this work that fuel adulteration in Jordan is carried out mainly by blending kerosene into regular gasoline. The price of kerosene in Jordan is much less than that of gasoline. This encourages greedy dealers to practice this illegal act. In this research, the fractional distillation analytical methods were utilized for detecting regular gasoline adulteration methods of analysis have been optimized, samples have been collected from different gas stations in northern Jordan and then tested. The method of analysis was simple, less expensive and very comparable to other high sophisticated techniques.

Keywords: Gasoline, Kerosene, Distillation Petroleum, Distillation Curve

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INTRODUCTION

Gasoline is a mixture of more than four hundred volatile and flammable liquid hydrocarbons ranging from 4 to 12 carbon atoms per molecule [1][2]. The liquid phase does not burn, only the vapors do. Gasoline has a flash point of -7 °C and an auto ignition temperature of 307 °C [3]. It is a mixture of paraffinic, naphthenic, olefinic, and aromatic hydrocarbons. In addition to hydrocarbons, gasoline also contains small amounts of sulfur, atmospheric oxygen, and traces of nitrogen. This petroleum fraction distils within the temperature range of 30– 220 °C [4][5].

Gasoline is produced by blending different fuel streams coming from various production processes. Atmospheric straight run cuts together with products from catalytic reforming and cracking, isomerization etc. units are the most commonly used feeds for the production of the final gasoline. These fractions are referred to as gasoline components. The blend recipes are determined such that the properties' specifications of the final gasoline are met [6].

Gasoline is blended primarily to achieve physical specifications for boiling range, vapor pressure, oxidation stability, and octane with the goal being desirable engine performance, namely cold/hot starts, acceleration, knock, resistance to vapor lock, etc [7][8].A number of analytical techniques are available to detect gasoline adulteration as flash point, refractive index and density but in this paper we are interested in fractional distillation.

MATERIALS AND METHODS

Materials

The samples of regular gasoline, kerosene and the suspected samples were collected from different gas stations in Irbid governorate in northern Jordan; Irbid contains more than 175 gas stations which market most types of fuel such as regular gasoline, super gasoline, diesel and kerosene. These petroleum products are being supplied by Jordan Petroleum Refinery Company. So, in the same period, the samples of pure regular gasoline and pure domestic kerosene were taken directly from the Jordan Petroleum Refinery company. Samples of regular gasoline were collected from 16 randomly chosen gas stations in northern Jordan. Samples containers were pre-washed 1L glass bottles fitted with glass stoppers. The time of sampling and the gas stations symbol were documented, samples were then transported to the laboratory at Jordan University of Science and Technology (JUST) for investigation.

Sixteen gas stations have been given symbols G1, G2 …. , for gas station 1 and gas station 2…., respectively, S symbol represent pure regular gasoline standards collected directly from the Jordan petroleum refinery at the same date, then stored in a refrigerator for analysis. A series of standards kerosene gasoline solutions ranging from 0 to 10% v/v were prepared by adding the appropriate volume of kerosene to 100 ml volumetric flask and completed to the mark by standard regular gasoline as shown in table (1).

Methods

Pure regular gasoline, pure kerosene and purposely adulterated regular gasoline (standards) and samples were distilled using a fractional distillation method at the laboratories of Jordan University of Science and Technology by utilizing the ASTM D86 procedure. The apparatus employed in fractional distillation composed of a round bottom flask (250ml), fractional column, thermometer, condenser, distillation adaptors, two graduated cylinders and aluminum foil.

Installing fractional distillation apparatus should be correct; every part should be fixed tightly to prevent leakage. The fractional column was rolled by aluminum foil to minimize transferring heat from the column to the surroundings. The receiving graduated cylinder at the end of condenser was immersed in the beaker filled with cooled water. The tip of the condenser touches the inner wall of receiving graduated cylinder and it was covered by aluminum foil. A 100 ml of pure regular gasoline or pure kerosene or standard of adulterated regular gasoline was put in the round bottomed flask and heated slowly and continuously using a heating mantle. The process was observed carefully until the first drop of condensate fell from the lower end of the condenser tube, this was then recorded as the initial boiling point. The thermometer readings at 5% to 90% recovered were recorded until final boiling point. The distillation curves for standards and samples were constructed. To visualize the results better, the temperature should be on the Y-axis and the volume of the distillate on the X-axis. A distillation curve will clearly show the boiling point of each distillate of samples or standards and their respective percentage volumes.

To estimate the analytical precession and accuracy and to assure the proper quality of analytical results the following necessary measures were performed:

1) Replicate analysis for each sample by the same apparatus, method and conditions, to improve the quality of the result and reliability.
2) The results obtained by the fraction distillation method were compared to results from automatic distiller that it exists at the Jordan Petroleum Refinery Company to all samples.
3) Periodic testing of the pure regular gasoline standard was used for the unadulterated sample, pure kerosene and standards to verify reliability and reproducibility of apparatus and method.

RESULTS AND DISCUSSION

Five accurately blended regular gasoline standards were prepared in the laboratory in addition to pure regular gasoline and pure kerosene were primarily tested by the fractional distillation method. The distillation curves for each standard were constructed. Sixteen samples of the regular gasoline collected from randomly chosen gas stations in Irbid area were tested by fractional distillation. Their distillation curves compared to those of standards to find suspected samples

Fractional distillation curves for samples were constructed in the laboratory in Jordan University of Science and Technology at atmospheric pressure using instructions in American Society of Testing and Materials (ASTM) method D86. The relationship of temperature readings correspond to first drop , 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% and 95% of the distilled volume were plotted, this represented by figure (1) and table (1). The distillation curve can, in simple terms, be represented by three points: T10 relates to cold start ability, T50 relates to cold drivability and T90 relates to combustion chamber deposit, which represent the temperature at which 10, 50 and

90% vaporization of gasoline initial volume occurs as shown in table (2). These temperatures characterize the volatility of the fuel' light, medium and heavy fractions. These fractions, in turn, effect the engine's different operating regimes[9][10][11].

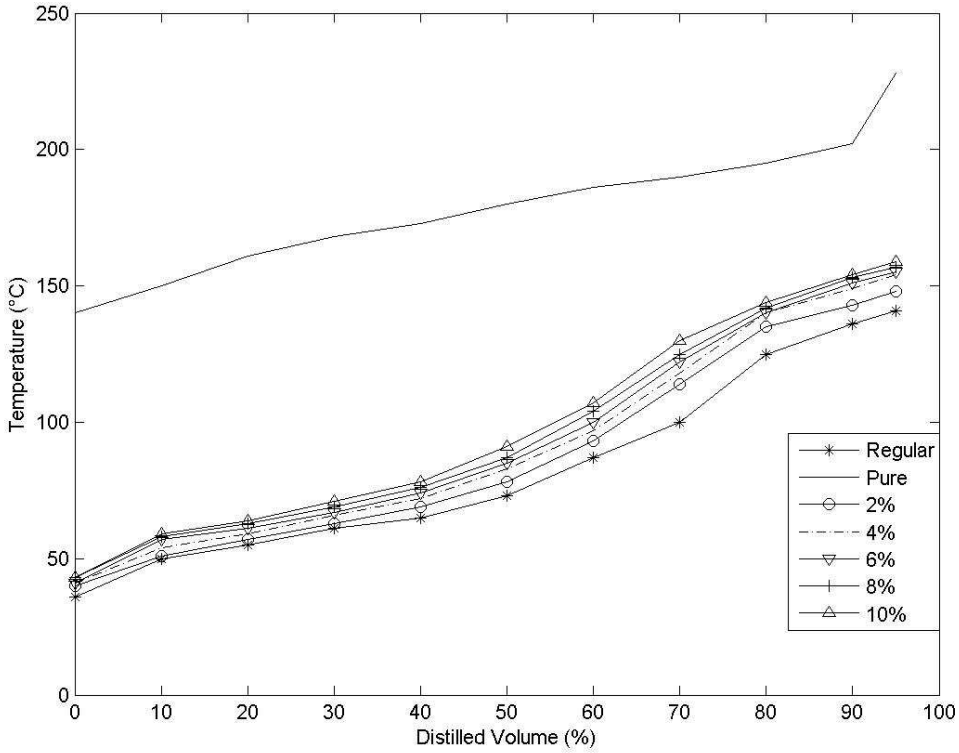

Figure 1 Distillation Curve for Standards.

Table 1 The Relationship Between the Temperatures and the Distilled Volume of all Standards.

Temperature °C (average)							
Distilled Volume (%)	Regular gasoline	Pure Kerosene	(2%). Standard	(4%). Standard	(6%). Standard	(8%). Standard	(10%). Standard
0%	36	140	40	41	41	43	43
10%	50	150	51	54	57	58	59
20%	55	161	57	59	61	63	64
30%	61	168	63	66	67	69	71
40%	65	173	69	72	74	76	78
50%	73	180	78	83	85	87	91
60%	87	186	93	97	100	104	107
70%	100	190	114	118	122	125	130
80%	125	195	135	140	140	142	144
90%	136	202	143	149	151	153	154
95%	141	228	148	154	155	157	159

Table 2 The Differences in the Results that Obtained by the Fractional Distillation among the Standards.

Characteristics	Standard (2%)	Standard (4%)	Standard (6%)	Standard (8%)	Standard (10%)
Initial boiling point (°C)	38 - 41	38 - 41	39 - 41	42 - 43	42 - 44
Temp at 10% distilled volume (°C)	50 - 52	52 - 54	55 - 57	57 - 60	58 - 60
Temp at 50% distilled volume (°C)	77- 80	82 - 85	84 - 87	86 - 89	89 - 91
Temp at 90% distilled volume (°C)	141 - 144	147 - 150	150 -152	152 - 155	153 - 155
Final boiling point (°C)	147 -149	153 - 155	154 - 156	157 - 158	158 - 160
Volume of the loss (ml)	3 to 4	3 to 4	3 to 4	2 to 3	2 to 3
Volume of total recovery (ml)	96 to 97	96 to 97	96 to 97	97 - 97.5	97 to 98
The volume of remained liquid (ml)	1 - 2	1 - 2	1 - 2	2 - 3	2 - 3

ASTM D86 is a creditable method that employed in the petroleum refineries for operation of the distillation towers is based on volatility and compositional data obtained from this D86 distillation. Also, gasoline specifications include the D86 boiling range. The distillation characteristics are critically important for both automotive and aviation gasoline, affecting starting, warm-up, and tendency to vapor lock at high operating temperature or at high

altitude, or both. The presence of high boiling point components in these and other fuels can significantly affect the degree of formation of solid combustion deposits [12][13].

Table 3 The Relationship Between the Temperature and the Distilled Volume of G8 Sample.

Distilled Volume (%)	Temperature °C
0%	42
10%	59
20%	64
30%	70
40%	78
50%	89
60%	106
70%	128
80%	142
90%	154
95%	159

Table 4 The Relationship Between the Temperature and the Distilled Volume of G15 Sample.

Distilled Volume (%)	Temperature °C
0%	43
10%	61
20%	65
30%	75
40%	79
50%	91
60%	110
70%	132
80%	145
90%	157
95%	162

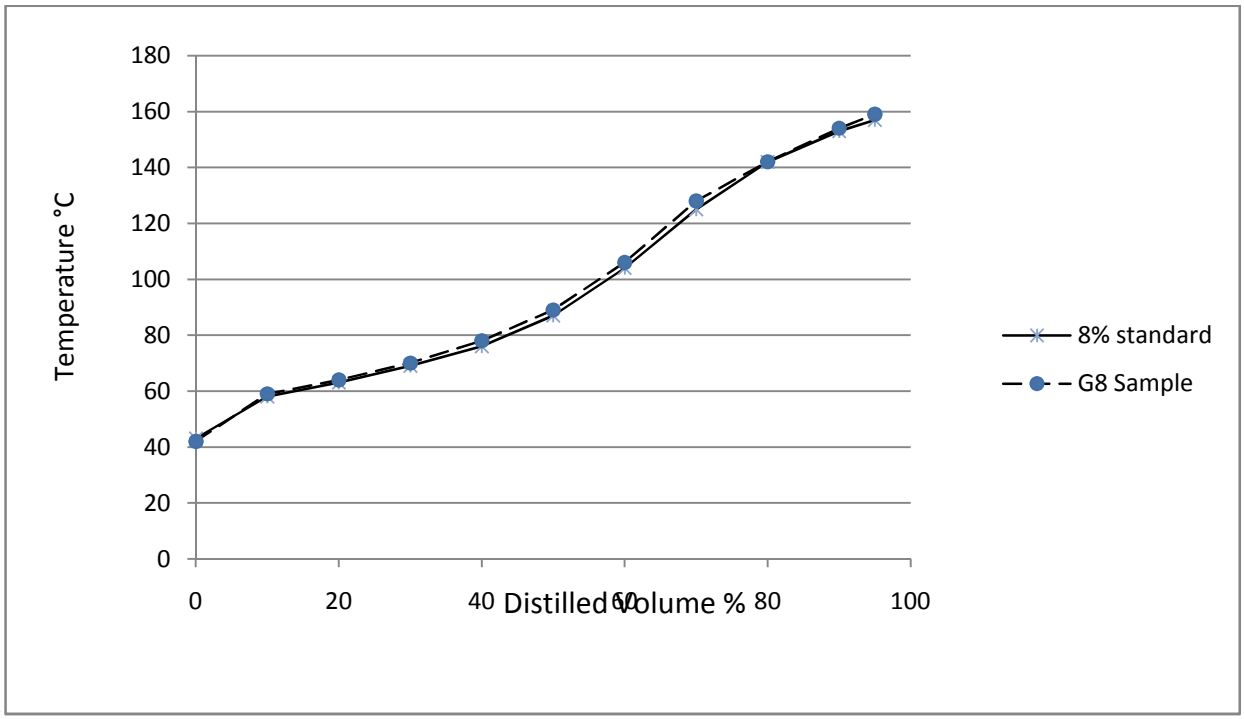

Figure 2 The Comparison Between 8% Standard and G8 Sample

The average initial boiling point of regular gasoline was nearly 36°C. It is the first drop fallen nearly after 5 to 7 minutes after heating started, The distillation process continued to 139°C, which is corresponds to 95% distilled volume. 139°C is the maximum temperature reached during distillation. After the distillation of the pure regular gasoline was finished, a dark yellow oily liquid remained in the flask with a volume of about 2 ml. This remaining

liquid was more viscous than regular gasoline. It did not evaporate even at higher temperatures. It converted to a dark brown or black color.

This residual liquid was formed by chemical degradation of the gasoline during the distillation process especially at high temperature; One important consequence of the degradation is the gum formation (polymerization of the olefins) that increases the average molecular weight of the hydrocarbons [14][15]. The major reasons to form the gum are olefins content and some catalytic factors at high temperatures. Leaded gasoline [14][15][16][17] has high olefin content, since its main components come from fluid catalytic cracking refinery units. In contrast; the olefin content in unleaded gasoline is relatively low.

The volume of the sample before the fractional distillation was 100 ml, and volume of the residue (gum) in distillation flask was nearly 3 ml, the total recovery from the test equaled 97 ml, the difference between the volume of the original sample and the total recovery which equivalent about 3 ml referred to volume loss.

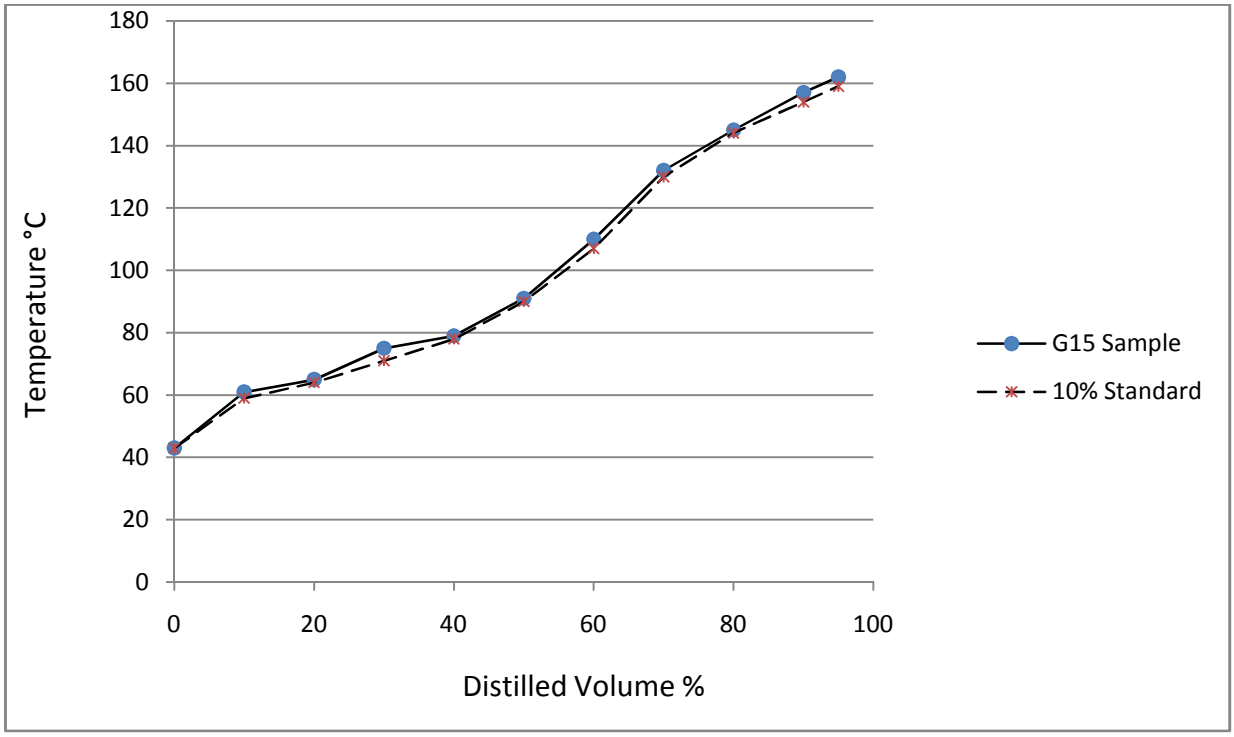

Figure 3 The Comparison Between 10% Standard and G15 Sample

The volatility of regular gasoline is very high because of the presence of low boiling point and high vapor pressure compounds such as butane and its isomer (BP -2°C) [19]. If the distillation is carried out at room temperature nearly 25°C this may lead to evaporation of some regular gasoline from a round bottomed flask, i.e. before beginning heating or before the temperature reaches an initial boiling point which needs at least 5 minutes. Kerosene is produced from the fractional distillation of crude oil and its boiling temperature range is 140–280°C. Chemically, it is composed of paraffin, naphthene and aromatic hydrocarbons; therefore, the composition of kerosene is very complex [18][19].

The samples of the pure kerosene were distilled in a laboratory by fractional distillation at an atmospheric pressure and room temperature, the initial boiling temperature was 140 °C (average). The time from first application of heat to initial boiling point was between 12-16 min. The overall time to complete distillation of the pure kerosene was about 70 minutes. The maximum thermometer reading during the distillation process was 228 °C, at this temperature the volume distilled approached 95%. Table (1) and figure (1) show relationships between the thermometer readings and the percentage evaporated. The volume of remaining liquid in the distillation flask was about 4.5 ml; its appearance and odor were similar to that formed by the distillation of the regular gasoline. The total recovery was up-to 99.5 ml. The amount of the loss was 0.5ml only, and the overall time of the distillation exceeded one hour. Table (4) represents the major differences between the pure kerosene and the pure regular gasoline distillations.

Tables (1 and 2) show the relationship between the temperature and distilled volume of standards and samples. Figure (1) illustrates the distillation curves of standards and samples. The same procedure is applied to each sample.

The results of fractional distillation analysis showed that G8 & G15 samples were adulterated as shown in tables (3, 4) , which indicate to the G8 sample was adulterated with the kerosene and its percentage nearly 8%. But G15 sample was adulterated with kerosene and its percentage is close to 10%, which assured by comparison between distillation curve of the samples and standards as illustrated in figures (2,3). These results were also confirmed by an octane number determination technique [7].

CONCLUSION

Results show that 2 samples out of 16 were suspect i.e. adulterated by 8% and 10 %. The fractional distillation method used in analysis is simple, cheap, accurate, precise and effective for detecting adulteration between 2 to 10%, but it failed to detect kerosene concentration in gasoline below 1%. The method needs simple apparatus that are available in most chemistry labs, but it is time consuming; it requires at least 40 min for each sample.

Acknowledgment
The authors acknowledge the support of Deanship of research, Jordan University of Science & Technology.

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