

Study of the research octane number depression of domestic kerosene-doped automotive gasoline

^{†a}Adnan A. Dahadha, ^bNesrin Talat and ^cSalem Barakat

^aDepartment of Applied Chemical Sciences, Jordan University of Science and Technology, Irbid, Jordan
^bDepartment of Mechanical Engineering, Friedrich Alexander Universität Erlangen-Nürnberg, Cauerstr. 4 D-91058, Germany
^cDepartment of Applied Chemical Sciences, Jordan University of Science and Technology, Irbid, Jordan

ABSTRACT

All engines are manufactured to run on specific gasoline, the engine problems will occur if the gasoline specifications is changed. When kerosene or diesel are added to various types of automotive gasoline, the octane rating quality will fall below the octane requirements of engine and therefore engine knocking can occur. knocking is a spontaneous and extremely rapid ignition of the gasoline-air mixture in the combustion chamber. The concurrent sudden build-up of high heat and pressure, far beyond that of normal combustion, creates a shock wave which is heard as a ping or a knock and causes damage to the engine and reduce the engine efficiency. A number of analytical techniques are available to detect gasoline adulteration as flash point, refractive index and density. But in this research, the effect of adding domestic kerosene to automotive gasoline on the research octane number rating was accurately studied and investigated to see the magnitude of an octane number depression then the research octane number calibration curves were constructed to detect some suspected samples of automotive gasoline that were collected from different stations in Jordan.

Keywords: Gasoline, Kerosene, Research Octane Number

INTRODUCTION

Gasoline is a mixture of liquid, volatile and inflammable petroleum-derived compounds, in the range of C₄–C₁₂ carbon atoms and boiling points in the range of 30 C–225 C. Many physical and chemical properties are utilized in quality-control tests for gasoline and these tests include measurement of relative density, temperatures equivalent to 10%, 50% and 90% distilled volume, final evaporation points, the flash point, octane numbers (MON and RON) [1][2][3].

Knocking occurs when the automotive gasoline burns prematurely in a cylinder or explodes in an internal combustion engine, causing a distinctive high sound which resembles knocking, or pinging. An octane number is a number which reflects a gasoline resistance to knocking. Engine knock can cause damage to the engine, and it indicates that the engine is not operating as efficiently [4]. Many engines are required to specific octane rating recommendations. Octane numbers are obtained by testing a gasoline in controlled conditions. Two various types of octane number can be obtained: the research octane number (RON) or motor octane number (MON) [5][6]. These numbers are obtained by testing gasoline in different circumstances, with the MON applying more stress on the engine to see how automotive gasoline perform in hard conditions. Two chemicals, heptane and iso-octane, are used to calibrate the scale, with heptane being zero, and iso-octane being 100, when a automotive gasoline is investigated in an engine, it is compared with a blend of heptane and iso-octane to see which blend most closely matches the fuel performance, if the blend includes 20% heptane and 80% iso-octane, for example, the fuel will have an octane number of 80. Octane numbers can be adjusted by putting additives in the fuel which will adjust the level of knock [7][8][9].

The increased demands on the high quality of automotive gasoline as indicated by its octane numbers (Research octane number or RON and Motor octane number or MON), among others, have been placed. The RON accounts for fuel performance under low severity engine operation while the MON for more severe operation that might be incurred at high speed or high load [5]. In practice the octane of a gasoline is reported as an Antiknock Index or Pump Octane which is the average of RON and MON. Both RON and MON are still determined in a standardized single cylinder, variable compression ratio (from 4:1 to 18:1), internal combustion engine following the standard methods ASTM D2699 [10] and D2700 [11], respectively. Most internal combustion automobile engines, whether they are four, six or eight cylinders, run on a four-stroke cycle known as the Otto cycle. The four strokes are: intake, compression, combustion and exhaust. To put it in the simplest of terms, each of the vehicle's pistons moves up and down within a cylinder. As the piston moves to the bottom of the cylinder, a mixture of fuel and air flows in, the piston then moves upward, toward the top of the cylinder, compressing the air and fuel mixture as it does so [12][13]. Both RON and MON are relative values based on accepted standard fuel mixtures. As long as this process works as described above, the engine runs smoothly. But occasionally the pressure of the piston itself will cause the air and gas mixture to ignite prematurely during the compression cycle, creating a smaller, less powerful explosion. This is called preignition and it's the cause of engine knock. The engine is operated at a constant speed (RPMs) for both RON and MON and the compression is increased until the onset of knocking. Engine speed is set at 600 rpm for RON and 900 rpm for MON. Petroleum industry has always been used empirical performance standards of its gasoline products, such as RON and MON. Only after gas chromatography became widely available, compositional standards and constraints on gasoline's composition have started to be applied [12][14][15][16].

MATERIALS AND METHODS

Materials

The Octane Number Instrument that available in Jordan Petroleum Refinery was employed to investigate the octane number for standards and samples. It holds these specifications: Range of measurement: 50~100 octane numbers, Range of compression ratio: 4:1~12:1, Inner diameter of cylinder: 65mm, Piston stroke: 100mm, Rotate speed of engine: 900±9r/min (MON) 600±6r/min (RON) and Power: 8000W.

Two types of automotive gasoline (regular gasoline 87 RON and super gasoline 95 RON), which series of standards kerosene gasoline solutions ranging from 0 to 10% v/v were prepared in the laboratory by adding the appropriate volume of kerosene to 100 ml volumetric flask and completed to the mark by standard regular and super gasoline types in addition to pure regular, pure super gasoline and pure kerosene, the source of standards and samples was Jordan Petroleum Refinery. 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. Pure regular and Pure super gasoline standards collected directly from the Jordan Petroleum Refinery at the same date, then stored in a refrigerator for analysis.

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 results and reliability.
- 2) Periodic testing of the pure regular and super gasoline standards were used for the unadulterated samples and the standards to verify reliability and reproducibility of apparatus and method.

Methods

A research octane number determination instrument is available at Jordan Petroleum Refinery laboratory. The determination based on comparing the knocking intensity of gasoline with standard mixtures of isooctane and n-heptane that would have the same anti-knocking capacity as the fuel under test: the percentage, by volume, of 2,2,4-trimethylpentane in that mixture is the octane number of the fuel. For example, gasoline with the same knocking intensity as a mixture of 87% isooctane (100 ON) and 13% (0 ON) heptane would have an octane rating of 87. A rating of 87 does not mean that the gasoline contains just iso-octane and heptane in these proportions, but that it has the same detonation resistance properties. The standards and samples were tested under same conditions by research octane number determination instrument, every standard and sample was tested more than once to obtain reproducible and accurate average reading research octane number rating.

RESULTS AND DISCUSSION

In Jordan , two main types of gasoline are sold in the service stations: regular gasoline with a Research Octane Number of 87 (87 RON) , and super gasoline with a Research Octane Number of 95 (95 RON) for newer cars. These two types are prone to adulteration especially with cheaper domestic kerosene leading to substantial changes in research octane number. According to tables 1 and 2 which show decreasing RON as amount the domestic kerosene in the regular and super gasoline standards increases, this can be attributed to composition and types of hydrocarbons present in the kerosene mixture.

Gasoline is a mixture of paraffinic, naphthenic, high concentration of olefinic, and aromatic hydrocarbons. Cracking, isomerization, and other processes can be used to increase the octane rating of gasoline to about 90. Anti-knock agents may be added to further increase the octane rating. Tetraethyl lead, $Pb(C_2H_5)_4$, was one such agent,. The switch to unleaded gasoline has required the addition of more expensive compounds, such as aromatics and highly branched alkanes, to maintain high octane number [17][18][19][20].

Regardless of the crude oil source or processing history, the major components of all kerosenes are branched and straight chain paraffins and naphthenes (cycloparaffins), which normally account for at least 70% by volume, aromatic hydrocarbons in this boiling range, such as alkylbenzenes (single ring) and alkylnaphthalenes (double ring) do not normally exceed 25% by volume of kerosene streams, olefins are usually not present at more than 5% by volume [14][21]. The flash point of kerosene is between 37 and 65 °C (100 and 150 °F), and its autoignition temperature is 220 °C (428 °F) [10]. As we know the RON of straight chain paraffins is very low such as n-hexane (ON = 24) , n-octane (ON= -19) and n-nonane (ON= -17) [22][23]. Thus the high concentrations of paraffines and naphthenes components in domestic kerosene bring down its research octane number. The effects of blending gasoline with domestic kerosene are increased density, decreased volatility and reduced octane rating [14].

Tables (1 and 2) and figures (1 and 2) exhibit the effect the domestic kerosene on research octane number rating of regular gasoline and super gasoline. When adding 2% of domestic kerosene to regular gasoline (87 ON) and super gasoline (95 ON), their original research octane number were clearly dropped to be 85.9 and 93.5, respectively. This indicates that domestic kerosene has a capability to reduce octane number even though its amount is small. 10% of kerosene depressed the research octane number to be 81.5 and 89.6 for regular and super gasoline respectively. To obtain the more reproducible and accurate data, the research octane number tests for standards of regular and super gasoline were repeated under same circumstances, then the readings were adopted precisely.

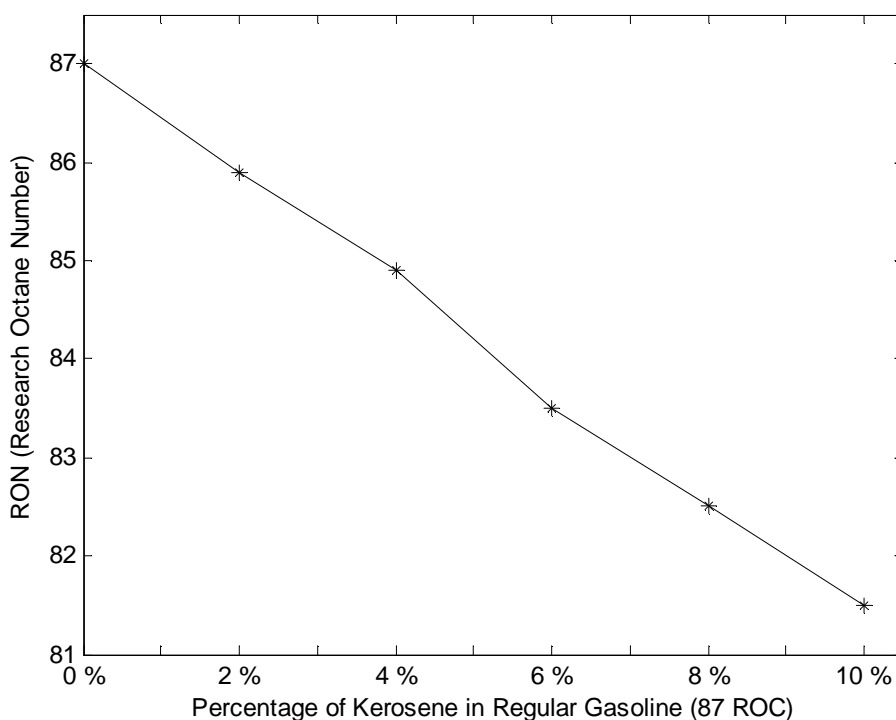


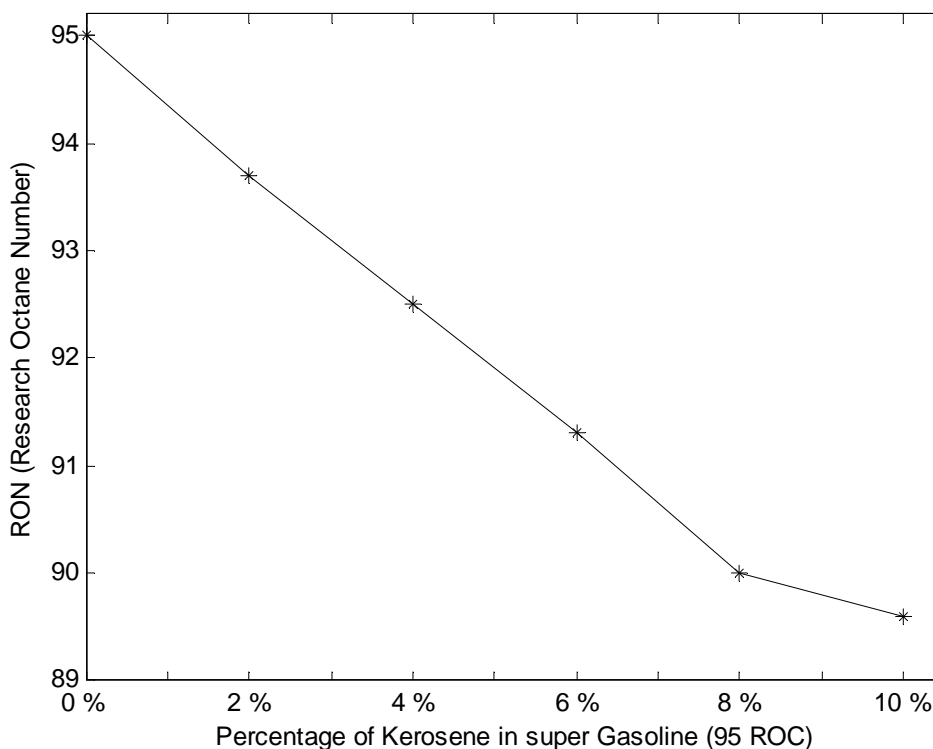
Figure 1: The Relationship Between the % Kerosene in Regular Gasoline and the Research Octane Number of Regular Gasoline

Table 1 : Research Octane Number of Standards for Regular Gasoline

| % Kerosene in Regular Gasoline | Research Octane Number |
|--------------------------------|------------------------|
| 0 | 87 |
| 2 | 85.5 |
| 4 | 84.5 |
| 6 | 83.5 |
| 8 | 82.5 |
| 10 | 81.5 |

Table 2 : Research Octane Number of Standards for Super Gasoline

| % Kerosene in Super Gasoline | Research Octane Number |
|------------------------------|------------------------|
| 0 | 95 |
| 2 | 93.5 |
| 4 | 92.5 |
| 6 | 91.5 |
| 8 | 90.0 |
| 10 | 89.5 |

**Figure 2: The Relationship Between the % Kerosene in Super Gasoline and the Research Octane Number of Super Gasoline**

As it is noticed that there was a logical and sequential dropping of research octane number of two types of automotive gasoline resulted from increasing amounts of the adulterant (domestic kerosene). This property was utilized to detect the adulteration and estimate its quantity. Although the Jordan Petroleum Refinery depends on a number of analytical techniques that available to detect gasoline adulteration as flash point, refractive index and density, gas chromatography- mass spectrometry and Fourier Transform Near Infrared or FT-NIR.

Calibration curves were constructed for standards of regular and super gasoline, which represents the research octane number of standards against the percentage of the domestic kerosene in the regular and super gasoline, this shown in figures (3 and 4). Samples were collected randomly from the gas stations in Irbid (northern region of Jordan) and tested by research octane number as illustrated by table 3. The quality and quantity of adulterant were estimated by the calibration curves.

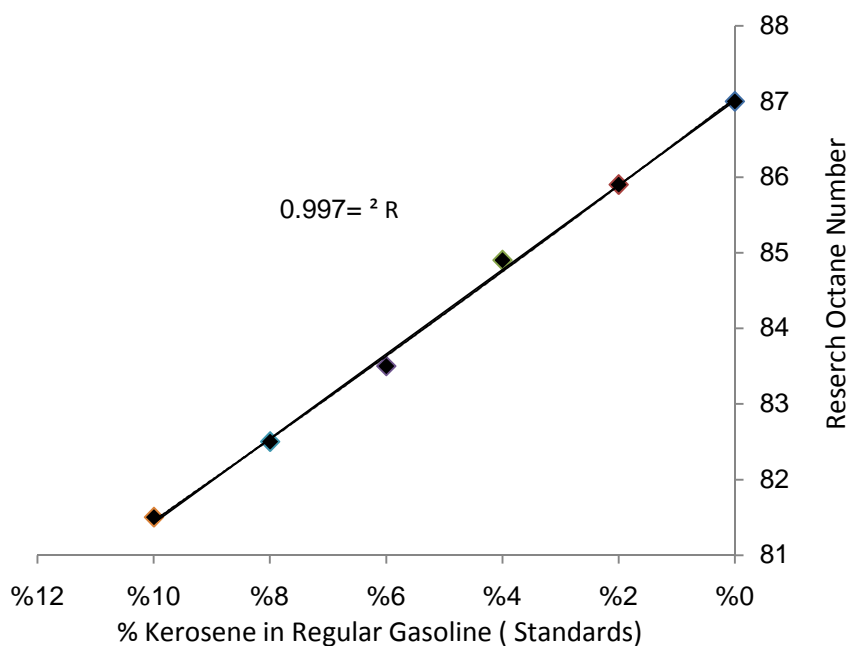


Figure 3 : Calibration Curve of Research Octane Number of Regular Gasoline Standards

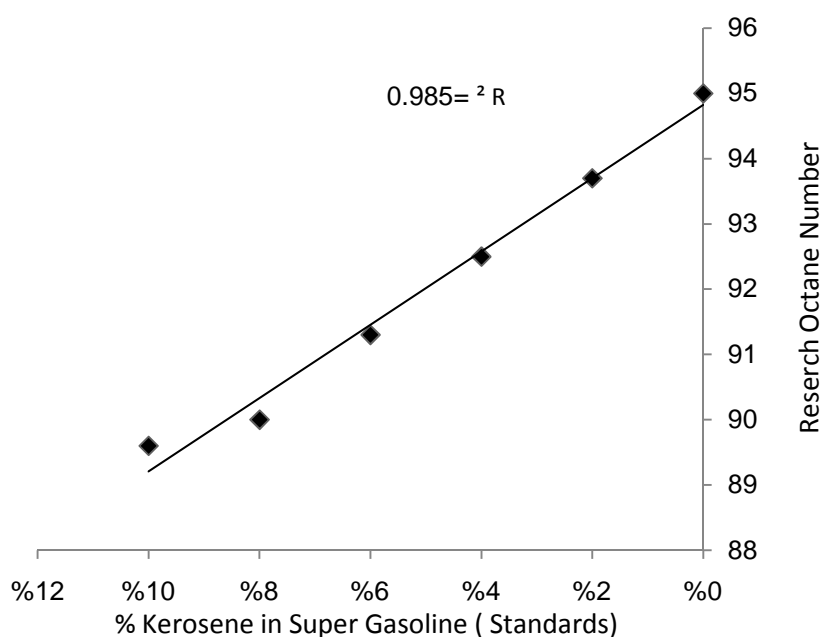


Figure 4 : Calibration Curve of Research Octane Number of Super Gasoline Standards

The results of research octane number analysis showed that G8 & G10 samples were adulterated as shown in tables (3) , which indicate to the G8 sample was adulterated with the kerosene and its percentage nearly 8%. But G10 sample was adulterated with kerosene and its percentage is close to 10%, which assured by calibration curve of the standards as illustrated in figures (3). Fortunately, super gasoline samples were an unadulterated. These results were also confirmed by an fractional distillation and density techniques.

Table 3 : Research Octane Number of the Samples

| Samples (Regular Gasoline) | Research Octane Number |
|----------------------------|------------------------|
| RG1 | 87 |
| RG2 | 87 |
| RG3 | 87 |
| RG4 | 87 |
| RG5 | 87 |
| RG6 | 86.5 |
| RG7 | 87 |
| RG8 | 82.5 |
| RG9 | 87 |
| RG10 | 80.5 |
| Samples (Super Gasoline) | Research Octane Number |
| SG1 | 95 |
| SG2 | 94,5 |
| SG3 | 95 |
| SG4 | 94.5 |
| SG5 | 95 |
| SG6 | 95 |
| SG7 | 94.5 |
| SG8 | 94.5 |
| SG9 | 95 |
| SG10 | 95 |

CONCLUSION

Results show that 2 samples out of 20 were suspect i.e. adulterated by 8% and 10 %. The research octane number method used in analysis is an accurate, fast and effective for detecting adulteration between 2 to 10%, but it needed to large amount of sample. The method is required to special apparatus that are available in Jordan Petroleum Refinery.

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