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A STUDY OF THE RELATIONSHIP BETWEEN THE OCTANE NUMBER AND THE CHEMICAL COMPOSITION OF REGULAR, MIDGRADE, AND PREMIUM GASOLINE

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ABSTRACT:

The present study was conducted at Zakho City in Northern Iraq to evaluate three different types of gasoline: Regular, Midgrade, and Premium. These types of gasoline are categorized based on their octane rating, which was measured to verify their classification. The results showed that the initial classification was accurate, with respective values of 87.5, 89.8, and 91.1.

The study evaluated the three grades of gasoline available at Zakho Gas Stations in Northern Iraq, including Regular, Midgrade, and Premium. The study also compared the chemical composition of the three gasoline grades in terms of aromatics, olefin, sulfur content, and oxygen content. All the three gasoline grades met the American Society for Testing and Materials (ASTM) standard for chemical composition, and all had acceptable specific gravities. In general, the study showed that the Regular and Premium gasoline types sold in the north of Iraq meet international quality standards. However, Midgrade gasoline is not recommended for use during the summer due to its high RVP value, low initial boiling point (IBP), and final boiling point (FBP), which can lead to increased volatility and environmental pollution, Moreover, using this type of gasoline may cause problems with the car engine.

KEYWORDS: Gasoline, Octane Number, Sulfur Content, Reid Vapor Pressure and Gasoline Distillation.

1. INTRODUCTION

The purpose of this study is to analyze the three different types of gasoline available at Zakho gas stations. The analysis includes a comparison of the composition, and amounts of additives present in each type, as well as the properties that differentiate them in terms of price and efficiency. Gasoline is a type of fuel made by refining petroleum. It is used primarily as fuel for internal combustion engines in automotive vehicles(Ferrari et al., 2022). It is composed of a complex mixture of hundreds of volatile and combustible compounds with 4-12 carbon atoms(Domask, 1984), as well as additives and blending agents(Kuppusamy et al., 2020). Gasoline composition varies depending on refining processes, crude oil used, and product demand(Husham, 2019). Gasoline does not have a single boiling point, but instead is made up of lighter fractions that begin to evaporate at temperatures between 32-38 (°C), and heavier fractions that evaporate at higher temperatures between 149-204 (°C). This creates a "distillation curve" which shows the different boiling points of the various components in gasoline(ASTM Standard D86-18, 2019) and (Spieksma, 1998).

In gasoline fuels, volatility, and octane number are among the most important parameters (Viskup, 2020). Gasoline, like other hydrocarbons, does not ignite in its liquid state, as it must first evaporate and mix with oxygen to ignite(Cheng et al., 1993). The self-ignition of fuel causes a knocking impact in gasoline engines(Husham, 2019). Octane number is the indicator that characterizes the resistance to the detonation of gasoline in the internal combustion engine, depending on the molecular structure, stability, material content, sulfur, etc.(Pasadakis et al., 2006).

Fuel self-detonation in the engine cylinder can cause pressure pulses, increased fuel consumption, loss of power, and even engine damage (Pulkrabek, n.d.). The most important methods to determine the octane number are Motor Octane Number (MON) (ASTM Standard D2700-23, 2009), Research Octane Number (RON) (ASTM Standard D2699, 2009), and Antiknock Index (AKI). The antiknock index (AKI) is defined as the arithmetic average of RON and MON values, according to ASTM D4814 (ASTM Standard D4814, 2010). while the research octane number (RON) is based on fuel composition. The MON method produces lower octane numbers due to higher post-combustion temperature and lower compression ratios than the RON method(Oseev et al., 2013) and (Viskup, 2020). The octane number is traditionally measured with expensive and impractical methods. Instead, multivariate calibration with infrared analysis has been found effective in determining MON and RON, as well as other properties of automotive fuels (Fodor et al., 1999), (Oliveira et al., 2004), and (Mendes et al., 2012).

The volatility of gasoline fuels is typically quantified by measurement of Reid Vapor Pressure (RVP)(Gaspar et al., 2019) is a critical characteristic of gasoline, high RVP compounds are needed for vehicle starting and warm-up for spark-ignition n. RVP is controlled to reduce vapor lock concerns for fuel systems(Blumberg et al., 2003) and (Udo et al., 2020). RVP is the most important indicator both volatility and emissions because of the relation of the existing volatile organic compounds in fuels (Babazadeh Shayan et al., 2012).

2. MATERIALS AND METHODS

In this study, three types of gasoline with a difference in their octane number are collected from different oil stations in Zakho, Iraq. The gasoline samples were stored in appropriate polyethylene bottles, sealed, and refrigerated to 8-15 (˚C) to prevent the loss of volatile components until all required analyses were performed accurately(Mendes et al., 2012), and (Mendes et al., 2017).

Research and motor Octane Number determined by Shatox Sx-100 M portable Octane / Cetane Analyzer, Russia for the three gasoline samples. It takes a maximum of 10 seconds to detect the gasoline type. The process is fully automated, with the operator

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only needing to fill the sensor with gasoline, switch on the instrument, and record the results from the display. The Octane Meter is user-friendly, requiring no regular adjustments or special maintenance. It works by measuring the dielectric properties of the sample and comparing the results to the parameters stored in its internal program(Karim, 2015) and (Amin, Fanar, 2011). The results are indicated in Table 1.

Gasoline components, including Aromatics, Benzene, Toluene, Olefins, Total sulfur content, Oxygen Content, Ethanol (C_2H_5OH), Methanol (CH_3OH), and Methyl tert-butyl ether (MTBE), were determined using an ERASPEC FTIR Spectrometer Fuel analyzer from eralytics GmbH, Austria, according to specific ASTM standards for each test. Table 2 displays all the results and standard values.

The Pyknometer Method (IP 190 ASTM D 1217) determines density. Specific Gravity (Sp.gr) is the ratio of the sample density at 15.15°C (60°F) to water density at the same temperature(Hoffman, 1992). API can be calculated using an equation(L. M. Ahmed, 2007).

$$\boldsymbol{API = \frac{141.5}{Sp.gr\ (at\ 15.5^{\circ}C)} - 131.5}$$

Winter and summer RVP samples were measured using the ERAVAP Vapor Pressure tester from eralytics GmbH, Austria, according to ASTM 5191. Results are show in Table 3.

Preliminary Distillation at atmospheric pressure is a method of separating mixtures based on differences in their volatilities in a boiling liquid mixture. The D86 standardizes the atmospheric pressure distillation test using a laboratory distillation unit to determine the characteristics of the boiling range of gasoline quantitatively. Without using fractionating columns, 100 ml for each gasoline sample is distilled in a 250 ml round bottom flask under prescribed conditions of heat input and rate of distillation. The temperature records after 10%, 50%, and 90% of the sample volume are distillate, as well as the initial and final boiling point (Santos et al., 2021), (Spieksma, 1998), and (Mendes et al., 2012). The aim of this test is to determine if the light and heavy proportions of fuel produced are appropriate for optimal combustion and to examine the relationship between the type of hydrocarbons and octane number. Results are shown in Table 4.

3. RESULTS AND DISCUSSIONS:

All results from the experiments are presented in Tables 1 to 4. Table 1 shows the values of RON, MON, and AKI for each gasoline sample. The ASTM Standard value is used to compare these values and determine whether the sample is Regular, Midgrade, or Premium gasoline. The results of the Octane Number analysis indicate that all three types fall within the standard range for their respective types, which are 87, 89-90, and 91-94(Have et al., 1990).

The minimum octane rating required for an internal combustion engine is 91(ÇANAKCI, 2004). Regular and midgrade gasoline can cause engine knock, especially in modern improved engines. Low-octane gasoline is a major issue, particularly for new high-compression engine vehicles. Premium gasoline has an octane rating that ensures the best performance for an internal combustion engine. Accrdingly , it is most recommended for high compression (or turbo) engines(Rodríguez-Fernández et al., 2020).

Table 1: Results of (RON), (MON), and (AKI) and ASTM Standard Value.

	RON	MON	AKI	ASTM Standard
Regular	91.5	83.5	87.5	87
Midgrade	94.9	84.7	89.9	89-90
Premium	96.9	85.4	91.1	91-94

Aromatic compounds such as benzene, toluene, and xylene have a high octane rating of over 100 and can be easily converted to water and carbon dioxide through complete combustion. However, these compounds are also harmful and carcinogenic, and their high volatility makes them dangerous as they can easily be transmitted to humans through smell(B. S. Ahmed et al., 2022) and (El-Naggar & Al Majthoub, 2013). According to ASTM D6277, Regular, Midgrade, and Premium gasoline contained 30.6%, 28.5%, and 31.6% volume of aromatic compounds, respectively Table 2. After comparing the samples to the maximum allowable limit of 35 vol.% according to the ASTM standard, it was determined that all three samples contained acceptable levels of aromatic compounds(“The Focus on Aromatics in Automotive Fuels Specifications,” 2002) and (Graf et al., 2023). This refers to all the aromatic compounds that were found in the gasoline samples.

Benzene and toluene are among the most important aromatics compounds that are present in the composition of gasoline samples. Benzene is used as an anti-knock agent in gasoline, but its concentration is now restricted to 1 vol.% or lower due to its carcinogenic and polluting properties (Verma & Des Tombe, 2002). Based on the data presented in Table 2, it can be observed that the benzene volume percentage of Regular, Midgrade, and Premium gasoline is 0.81, 0.54, and 0.43 respectively. These values fall within the acceptable range, indicating that all three samples meet the required standards.

Toluene is a type of benzene with one substitution, and its chemical formula is (C_7H_8). It can be found in gasoline either naturally during the refining process or added as an additive(Houtchens, 2009) and (Ezeldin, 2015). **Table 4** displays the volume percentage of toluene in Regular, Midgrade, and Premium gasoline, which are 8.04, 7.85, and 8.06 respectively. These values are within the acceptable range of ASTM Standard, which is 30 vol. % or lower(Leveque et al., 1994).

Olefins are hydrocarbons containing double bonds that improve the performance of gasoline. However, a high olefin content can increase emissions that contribute to the formation of ozone (Hochhauser, 2009) and engine deposits(Yitao et al., 2009). To reduce smog, it is important to decrease the olefin content(Hajbabaei et al., 2013). According to the ASTM Standard, the maximum volume percentage of Olefins is limited to 21% and 18% for regular unleaded and premium unleaded, respectively(Government of INDIA, 2014). Table 2 indicates the results of the examination of three gasoline samples to determine their Olefin volume percentage. The Regular and Midgrade gasoline samples had either 0% volume of Olefins or only trace amounts that were undetectable by the testing device. On the other hand, the Premium gasoline sample had a volume of 3.0%. The test results indicate that the values obtained are significantly lower than the ASTM Standard value. However, reducing the olefin content of a fuel and substituting it with paraffin can reduce the reactivity of the fuel, which can lead to incomplete combustion(Hajbabaei et al., 2013).

Total Sulfur, which refers to the combined amount of organic and inorganic sulfur compounds. Table 2 shows the result of the total sulfur content analyses; the Premium gasoline has the highest sulfur content of 97 ppm, wt. followed by Midgrade gasoline 68 ppm, wt. and Regular gasoline has the lowest 45 ppm, wt. the tests are performed to determine the total sulfur content in the three samples following ASTM D4294. The ASTM standard limits the total sulfur content in gasoline due to its toxicity and environmental hazards (Wormsbecher et al., 1993) to a maximum value of 100 ppm wt.(ASTM D4294 -08a, 2010).

The results indicate that the sulfur contents of the three samples fall within the ASTM standard value. however, some European countries mandate that sulfur in gasoline should be kept as low as 10 ppm (Faruq et al., 2012).

Gasoline's octane number is improved by adding oxygenated compounds like ethers and alcohols. In some countries, up to 20% of gasoline blends are oxygenates for safety and environmental friendliness(Aboul-Fotouh et al., 2019), (Reese & Kimbrough, 1993), (Siu et al., 2005), and (Faruq et al., 2012).

Table 2 displays the results for oxygen content in three gasoline samples tested according to ASTM D5845 by Infrared Spectroscopy, including Methyl *tert*-butyl ether (MTBE), and Ethanol. The oxygen content of premium gasoline is 1.80 mass%, while midgrade and regular gasoline have 1.39 mass%. According to the ASTM standard, the maximum allowable oxygen content in gasoline is 3.7 mass% (D'andrea et al., 2004). The data presented encompasses all of the oxygenated compounds that were detected in the gasoline samples. The results of all samples that represent less than half of the acceptable amount are included. Although oxygenated gasoline can reduce emissions and improve fuel economy, it can cause engine corrosion and reduce mileage(Martini et al., 2013) and (Allmägi et al., 2023).

Ethanol and MTBE are important examples of oxygen compounds present in the composition of gasoline samples. Since oxygen mass content in an ethanol molecule is approximately twice that of MTBE, less ethanol is required to meet specified oxygen content in fuel(Harley et al., 2000) and (Yao et al., 2009). Table 2 displays the volume percentage of ethanol content in Regular, Midgrade, and Premium gasoline as 1.99%, 2.82%, and 2.01%, respectively. According to the ASTM standard, the maximum allowable ethanol content in gasoline is 5 volume percentage as a maximum, all samples fall within the acceptable range. It's worth noting that adding ethanol to gasoline leads to increases in Reid vapor pressure(Pumphrey et al., 2000) and (Zhang et al., 2023), and alters the fuel's distillation curve and composition (Hsieh et al., 2002).

The results for the volume percentage of Methyl tert-butyl ether (MTBE) content in Regular, Midgrade, and Premium gasoline are presented in Table 2. The values for these gasoline types are 3.20, 3.15, and 6.05, respectively. It is noteworthy that Premium gasoline contains approximately twice as much MTBE as Regular and Midgrade gasoline. The maximum volume percentage allowed by ASTM Standard is 15. MTBE was previously used as an additive in gasoline, but its usage has now been prohibited due to health concerns. currently, Ethanol is the preferred alternative to use as a gasoline additive (Koehl et al., 1991), (Zervas et al., 2002), and(Chong-Lin Song et al., 2006).

Table 3 gives results of specific gravity (Sp.gr.) at 15.5˚C, All the values obtained also fall within the standard range of 0.715-0.775. Premium gasoline with 0.760 has the highest value of Sp. Gr (at 15.5˚C) compared to Midgrade gasoline with 0.744 and Regular gasoline with 0.755(Stauffer et al., 2008). Therefore, from the (Sp.gr.) result the gasolines are not expected to cause any problem in usage.

Table 2: Results of Compositional Analysis by ERASPEC FTIR spectrometer

	Unit	ASTM	Regular	Midgrade	Premium	ASTM Standard
Aromatics	vol.%	D6277	30.6	28.5	31.6	35 max
Benzene C_6H_6	vol.%	D6277	0.81	0.54	0.43	1 max
Toluene	vol.%	D6277	8.04	7.85	8.06	30 max
Olefins	vol.%	D6277	0	0	3.0	18 max
Total sulfur content	ppm, wt.	D4294	45	68	97	100 max
Oxygen Content	mass%	D5845	1.39	1.39	1.80	3.7 max
Ethanol (C_2H_5OH)	vol.%	D5845	1.99	3. 12	2.01	5 max
Methyl tertiary butyl ether (MTBE)	vol.%	D5845	3.20	3.52	6.05	15 max

While the sp.gr is related to the American Petroleum Institute (API) of the gasoline sample. Table 3 displays the API values for Premium, Midgrade, and Regular gasoline, which are 54.7, 58.7, and 55.9 respectively. As the sample becomes heavy the API value decreases. Consequently, it is reasonable to see that the sample with the heaviest components has the lowest API value(Aboul-Fotouh et al., 2019). Among the three samples of gasoline, Midgrade gasoline has the highest API value, indicating that it is the lightest. On the other hand, Premium gasoline has the lowest API value, implying that it is the heaviest. According to the ASTM standard, the API values of the three gasoline samples fall under the "light type" category, which is the preferred category for API values equal to or greater than 30 (Viskup, 2020) and (Moro et al., 2023).

Table 3 presents the Reid Vapor Pressure (RVP) values in kilopascals (kPa) for each gasoline sample. The ASTM Standard specifies that for Iraqi weather, the RVP range should be between 49-82 for winter and 44-60 for summer(Dawood & Ismayyir, 2023). However, this study was conducted during the summer season. Gasoline with a higher RVP value is more volatile (Stewart & Arnold, 2009). Midgrade gasoline has the highest value at 60.7, indicating that it has more volatile compounds due to its higher ethanol content(Chong-Lin Song et al., 2006), and lower sp.gr value. This characteristic may not be ideal for the hot weather in Iraq. Gasoline with a high RVP value can cause vapor locks in internal combustion engines, as well as being lost to vaporization, which increases the risk of fire. On the other hand, Premium gasoline has a lower RVP value of 52.5 kPa, indicating that it contains fewer low volatile components than other grades. Regular gasoline has an RVP value of 54.0, which falls within the ASTM Standard values for summer.

Table 3: Results of Sp. Gr at 15.5˚C, API, and Reid Vapor Pressure (RVP) values

Properties	Regular	Midgrade	Premium	ASTM Standard
Sp. Gr (at 15.5˚C)	0.755	0.744	0.760	0.715-0.775
API	55.9	58.7	54.7	30 ≤
RVP (kPa)	54.0	60.7	52.5	49-82/44-60 Winter/Summer

Table 4 displays the boiling point characteristics in celsius of three gasoline samples and the ASTM Standard value. Hydrocarbon distillation characteristics have a significant effect on safety and performance. Boiling range provides information on fuel composition, properties, and behavior during storage and use. its determines the potential for explosive vapors, affecting starting, warm-up, and vapor lock. Distillation limits are included in product specifications, commercial contracts, and regulatory rules (ASTM Standard D86-18, 2019).

According to the ASTM Standard, the IBP values for the samples of Regular and Premium gasoline are acceptable, as they fall between 35-39(ASTM Standard D86-18, 2019). The Regular and Premium samples have IBP values of 36.1 and 38.8, respectively. However, the Midgrade gasoline sample has a lower IBP value of 30.1, which could cause fuel loss through evaporation especially in the extreme heat of North Iraq's summer climate that can go above 45˚C. This could contribute to air pollution, making it crucial to use gasoline with a higher IBP value (Kook & Pickett, 2010).

The temperature in (˚C) of recovery volume percentage of 10, 50, and 90 for each of the samples shows that the Regular and Premium gasoline have a value near the ASTM standard values (ASTM Standard D86-18, 2019). as the results are shown in Table 4.

Upon analyzing the samples, Final Boiling Point (FBP) values, it can be observed that the samples of Regular, Midgrade, and Premium gasoline have FBP values of 191.1, 185.9, and 191.3 ˚C, respectively. These all three values fall outside the ASTM Standard range of 195-204 ˚C(ASTM Standard D86-18, 2019), indicating that the samples contain very low amounts of heavy hydrocarbon compounds. This supports the reason for the high API value shown in Table 2.

When combining the RVP value results from Table 3 and the boiling range results from Table 4, for Midgrade gasoline, it becomes apparent that the Midgrade gasoline has values that are significantly different from the values selected in the ASTM Iraqi standard, as compared to Regular and Premium gasoline. This indicates that the Midgrade gasoline consists of components that are lighter than the required range and do not perform well in hotter temperatures. Therefore, for a better experience, it is recommended to use Regular or Premium gasoline in Iraq's hot weather

Generally, a liquid with a low boiling point has a high vapor pressure and is more likely to cause a fire. The vapor pressure of a liquid at a particular temperature determines how volatile it is and how low its boiling point is. Therefore, liquids with a lower boiling point are considered to be more volatile.

Gasoline with lower evaporation temperatures, which is more highly volatile, has some advantages, such as starting more easily, warming up better, and contributing less to deposits. However, it may also have some drawbacks, such as more fuel losses and an increased likelihood of vapor lock. If the boiling temperature of gasoline is too low, it may boil in fuel pumps, fuel lines, or carburetors when operating at high temperatures. This can cause a decrease in fuel flow to the engine, resulting in a loss of power, rough engine operation, or complete shutdown of the engine (Fodor et al., 1999) and (Mendes et al., 2017).

The data presented in Table 3 and Table 4 demonstrate that Premium and Regular gasoline are more suitable for summer use. In contrast, Midgrade gasoline is slightly higher than the ASTM standard value for the summer season.

Table 4: Results of Boiling Point Range at Atmospheric Pressure Distillation.

% Recovery	Temperature of Recovery (˚C)			ASTM Standard
	Regular	Midgrade	Premium	
IBP	36.1	30.1	38.8	35-39
10%	60.3	51.2	61.1	60
50%	109.8	99.1	110.1	110
90%	168.3	157.2	169.5	170
FBP	191.1	185.9	191.3	195-204

CONCLUSION

- It was found that the Regular, Midgrade, and Premium gasoline from the Zakho oil stations had octane numbers within the range for each of them.
- It has been found that the Regular and Midgrade samples do not contain any olefin compounds, whereas the Premium sample contains a small amount of it. To bring all three samples within the normal range as per the ASTM Standard, it is recommended and advisable to add some Olefin compounds.
- The oxygen content in the three samples is below the recommended value by the ASTM standard. In fact, it hasnot even reached half the recommended value. To bring all three samples within the normal range as per the standard, it is suggested to blend them with more oxygenated compounds.
-The gasoline sample classified as Premium gasoline possess a higher octane number due to higher aromatic, olefin, and oxygenated content; especially MTBE.
- Midgrade gasoline has a higher API and RVP value than regular and premium gasoline due to the increased blending of ethanol to improve its octane rating.
-Midgrade gasoline has a slightly higher RVP value than the ASTM Standard value.
- Midgrade gasoline has an Initial Boiling Point (IBP) lower than that selected by ASTM Standard value, while all samples have Final Boiling Point (FBP) lower than that selected by ASTM Standard value.
- Midgrade gasoline with high RVP, low IBP, and FBP does not meet ASTM standards, making it unsuitable for internal combustion engines. So it is not recommend to use as a fuel in internal combustion engine.

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