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Evaluating the Potential of n-Propyl Acetate as a New Oxygenate for Gasoline

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Abstract

Due to the depletion of oil and the rising demand for energy, numerous researchers are focusing on discovering alternatives to fossil fuels, some of which are capable of completely or partially replacing traditional fuels. Oxygenates are often blended partially with gasoline and diesel. The main goal of this work was to assess the potential of n-propyl acetate (NPA) as a new oxygenate to gasoline and to study its effect on gasoline properties. A total of six fuel blends were formulated for this study, involving the mixing of local gasoline with varying amounts of n-propyl acetate (0%, 2%, 4%, 6%, 8%, and 10%). For comparative purposes, a gasoline sample containing 10 volume percent of absolute ethanol was also examined in this study. The volatility properties of the fuel samples were assessed through various measurements, including: distillation curve and vapor pressure, in addition to some other calculated volatility properties. Some physical and chemical properties were also studied. The obtained results displayed that blending n-propyl acetate into gasoline hardly affects the volatility of gasoline. Incorporating n-propyl acetate into gasoline results in a slight reduction in vapor pressure, as 10% n-propyl acetate causes a decrease in vapor pressure by about 2 kPa. Also, n-propyl acetate hardly affects the distillation curve of gasoline as the values of T10, T50, and T90 changed insignificantly.

Keywords: Gasoline; n-Propyl acetate (NPA); Ethanol; Volatility Criteria; Physicochemical properties.

1.Introduction

Petroleum is a depletable resource of energy, and its depletion is a concern for many people around the world. As petroleum is extracted and used for fuel and other purposes, the amount of available oil in the ground decreases. Some estimates suggest that we may reach a peak in global oil production within the next few decades, after which the amount of oil available will begin to decline [1], [2].

The depletion of petroleum has several consequences, including rising prices for oil and related products, increased dependence on alternative sources of energy, and potential geopolitical conflicts over access to remaining oil reserves. To mitigate these effects, many countries around the world are prioritizing the development of alternative energy sources, including wind and solar power. Additionally, efforts are being made to enhance energy efficiency and decrease dependence on non-renewable fuels [3].

Oxygenated fuel blends are gasoline blends that contain oxygenates. The use of oxygenated fuels can contribute to decreasing our reliance on fossil fuels. Oxygenates are chemical compounds contain oxygen atoms in their chemical composition. Blending oxygenates into gasoline raises the oxygen content [4]. Oxygenates are often added to gasoline for two primary reasons: to enhance the fuel's performance and to improve combustion efficiency, resulting in a reduction of harmful pollutants released during combustion, particularly carbon monoxide and volatile organic compound[5][6][7][8].

Additionally, Oxygenates can potentially increase gasoline reserves by improving fuel efficiency and extending the amount of the fuel[9]. The most common oxygenates used in gasoline

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blends are ethanol and methyl tert-butyl ether (MTBE)[10]. Ethanol is a renewable fuel made from corn, sugarcane, or other plant material [11], while MTBE is a synthetic compound produced from methanol and isobutylene [12]. Ethanol is the most commonly used oxygenate in gasoline blends in the United States, and it is typically blended at a concentration of up to 10% (known as E10)[13][14]. Ethanol can also be blended at higher concentrations, such as E15 or E85, but these blends are less common due to concerns over compatibility with existing vehicles and fueling infrastructure [15].

MTBE was once a popular oxygenate [16], but its use has declined in recent years due to concerns over groundwater contamination from leaking underground storage tanks [17]. Many states have forbidden the use of MTBE in gasoline blends or have restricted its use [18] [19]. Other oxygenates, such as ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), and iso-butanol, are also used in some gasoline blends [20][21]. However, their use is less common than ethanol due to higher costs and limited availability [22]. Using oxygenated fuel blends in gasoline-powered vehicles can be beneficial in reducing the emission of harmful pollutants [6], [23]–[25][26][27]. However, it is crucial to consider the type and amount of oxygenate used, as it can significantly affect fuel efficiency, engine performance, and environmental consequences [28][29]. Currently, there is ongoing research to develop new oxygenates that can be used as fuels or fuel additives. Some of the promising candidates include: dimethyl ether (DME), bio-methanol, ethyl levulinate, isobutanol, methyl acetate, ethyl acetate, dimethyl carbonate, .ect [29][5], [30][31][32].

The aim of our current research is to explore the potential of n-propyl acetate as a new additive to gasoline fuel. n-propyl acetate is an organic compound that belongs to the ester group. It is a clear, colorless liquid with a fruity odor and is considered to have low toxicity. It is commonly used as a solvent for various applications such as coatings, inks, and fragrances. It can also be used as a flavoring agent in the food industry. Its chemical formula is $C5H_{10}O_2$, and it is typically produced on an industrial scale through the process of esterification, which involves the reaction between acetic acid and n-propanol [33],[34]. However, it is possible to produce propyl acetate from biomass-derived feedstocks, such as bio-propanol, in a process called bio-based production. In this case, propyl acetate can be considered partially renewable. The esterification reaction can be catalyzed effectively either homogeneously (e.g., using mineral acids) or heterogenously (e.g., using ion exchangers). Amberlyst 15 is a widely used catalyst for esterification reaction as it has the following advantages: (1) it is not corrosive (2) the side reactions are reduced (3) It can be readily separated from the reaction mixture [33]. In 2019, the global market size for n-Propyl acetate was 297.12 million USD. It is expected to reach 357.09 million USD by 2026, displaying a compound annual growth rate of 5.55% from 2020 to 2026[35].

The aim of the presented study is to explore the potential of n-propyl acetate (NPA) as a new oxygenated additive for gasoline. The research involves studying the impact of blending n-propyl acetate into gasoline fuel on various physical and chemical properties, including density, viscosity, calorific value, and oxidation stability. The study also encompasses an evaluation of its effect on volatility parameters, including the distillation curve, vapor pressure, T(v/l=20) and driveability index. Additionally, the study aims to compare the effects of ethanol and n-propyl acetate on gasoline properties so an E10 fuel blend was examined.

2.Experimental

2.1. Preparation of fuel samples

The gasoline sample used in the study was obtained from Cairo Petroleum Company, Egypt. n-propyl acetate (NPA) (99% purity) was purchased from Alfa Aesar, while Ethanol (99.9% purity) was purchased from Carlo Erpa Co. The fuel samples (G, NPA2, NPA4, NPA6, NPA8, and NPA10) were formulated by adding varying amounts of n-propyl acetate (0%, 2%, 4%, 6%, 8%, and 10%) to gasoline, respectively. E10 fuel blend was prepared by blending 10 vol% ethanol into gasoline. Table 1 contains the composition and properties of the tested fuel blends.

2.2. Characterization of fuel samples

The distillation process was carried out in accordance with ASTM-D86, while the vapor pressure was determined in accordance with ASTM-D5191. The area under the distillation curves was calculated using calculus, as previously described in other studies [36].

The driveability index (DI) was determined using the following correlation:

$DI=1.5*T10+3.0*T50+1.0*T90$

While the temperature of V/L=20 was estimated in accordance to the following equation:

$TV/L=20 = [52.47 - 0.33(VP)] + 0.20\ T10 + 0.17\ T50$ [37].

Where: VP is the vapor pressure in kPa, T10 and T50 in °C.

Table 2 gives the standard values of the volatility parameters of gasoline as approved by ASTM-D4814.

Composition (ml)	**G**	**E10**	**NPA2**	**NPA4**	**NPA6**	**NPA8**	**NPA10**
Gasoline	100	90	98	96	94	92	90
NPA	0	-	2	4	6	8	10
Ethanol	-	10	-	-	-	-	-
Total	100	100	100	100	100	100	100
Distillation data							
IBP,°C	40.6	41.92	36.27	37.52	37.28	39.04	37.59
T5,°C	55.74	50.98	53.2	53.53	54.39	55.78	54.88
T10, °C	59.59	53	57.4	57.78	58.65	59.84	59.25
T15,°C	62.63	54.83	60.71	60.91	61.72	62.97	62.57
T20, °C	65.74	56.28	63.66	64	64.95	65.81	65.83
T30, °C	71.21	59.48	70.03	70.39	71.31	71.66	72.2
T40, °C	77.87	62.78	77.3	77.46	77.92	78.22	78.98
T50, °C	85.54	66.35	85.28	85.31	85.46	85.36	86.5
T60, °C	94.53	87.57	94.33	93.85	92.97	93.39	94.16
T70, °C	106.1	101.92	104.9	103.49	103.03	102.47	102.53
T80, °C	120.93	116.83	119.23	117.46	115.8	114.29	114.29
T85,°C	132.07	126.86	129.95	127.8	126.42	124.66	124.38
T90, °C	148.23	142.99	146.22	143.85	143.09	141.59	141.94
T95, °C	185.39	173.2	182.92	178.21	173.51	169.59	174.77
FBP, °C	202.25	197.11	196.39	199.16	195.46	197.25	198.17
VP(kPa)	56.95	62.1	56.2	55.6	55.35	55.15	55.15
DI	494.23	-	488.16	486.45	487.44	487.43	490.31
$T_{(v/l=20)}$, °C	60.13	53.85	59.9	60.18	60.46	60.74	60.82
T10	59.59	53	57.4	57.78	58.65	59.84	59.25
T50	85.54	66.35	85.28	85.31	85.46	85.36	86.5
T90	148.23	126.86	146.22	143.85	143.09	141.59	141.94
AUDC, Square units	72.39	64.5	71.49	71.12	71.06	71.03	71.3

Table 1: Composition and properties of the fuel blends.

Table 2: Standards of the volatility parameters

Parameter (units)	Minimum	Maximum	Standard
RVP (kPa)	-	79	ASTM 4814
T10 , °C	-	60	ASTM 4814
T50, , °C	77	116	ASTM 4814
T90, °C	-	185	ASTM 4814
RVP(kPa)	50	80	EN228
DI	375	610	ASTM 4814
$T_{(V/L=20)}$, °C	35	55	ASTM 4814

3. Results and Discussion

3.1. Volatility criteria

Volatility is a vital parameter in the gasoline industry. Gasoline must convert from liquid state to vapor state for the combustion process in the engine. Therefore, the gasoline must meet the standards of volatility characteristics adopted in the country.

3.1.1. Vapor pressure

ASTM-D5191 is a quick and precise method for measuring the vapor pressure of the petroleum products. The Environmental Protection Agency (EPA) regulates the volatility of gasoline by establishing vapor pressure limits based on the season and geographical location. These limits aim to control the amount of evaporative emissions released into the atmosphere, which can contribute to air pollution and negative health effects. These limits control the volatile organic compounds emissions especially in hot weather. Also, gasoline must be formulated in such a way that ensures good engine startability in cold weather. The obtained results as displayed in Figure 1 show that addition of n-propyl acetate slightly decrease the vapour pressure of gasoline. The obtained results show that incorporation of 10% n-propyl acetate into gasoline results in a reduction of approximately 2.3 kPa in vapor pressure.

3.1.2. Distillation curve

The distillation curve is a very important parameter for gasoline industry. It is obtained by performing a distillation test for the fuel blends. The distillation curve is constructed by measuring the temperature at which a certain volume of vapor is collected during the distillation process.

It provides information on the composition of the fuel sample and can help predict its behavior under different conditions, such as high temperature or pressure. The distillation curve is composed of three regions; front-end, mid-range and tail-end. T10, T50, and T90 are the three most significant temperature points used to characterize the distillation curve of a fuel and represent the three regions in the distillation curve, respectively. They are the temperature degrees at which 10, 50, and 90 vol% of the petroleum product has been distilled, respectively. T10 is an important parameter because it provides information on the lightest and most volatile components of gasoline.

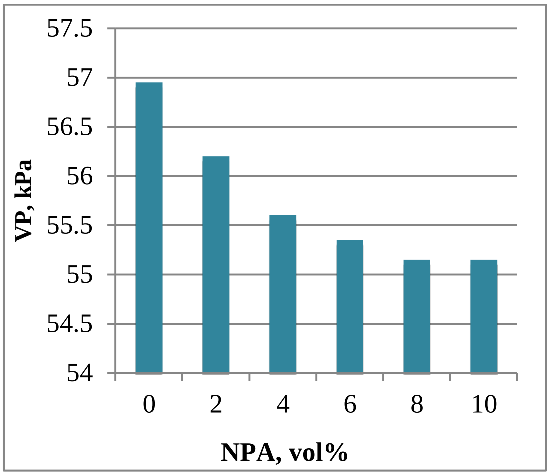

Figure 1: The effect of NPA addition on the vapor pressure of gasoline

Gasoline with a lower T10 value has a higher proportion of light fraction which can enhance engine performance but can increase evaporative emission and vapor lock in hot weather. To ensure good cold starts and prevent evaporative emissions and vapor lock during the summer season, it is important to regulate T10 value of gasoline. T50 represents the midpoint of the fuel's volatility range. Regulating this value is also important as it is crucial for maintaining a balance between low and high boiling constituents of gasoline. Carefully controlled T50 can help optimize the fuel's performance. Gasoline with a low T50 is more volatile which can lead to enhanced engine performance, warming-up, and acceleration. T90 value can vary depending on the specific refining process used to produce gasoline and the intended use of the fuel. T90 gives information on the amount of the long chain hydrocarbon present in gasoline which is important for fuel economy [38].

Figure 2 illustrates the impact of various concentrations of n-propyl acetate on the distillation curve of gasoline. The Figure shows that NPA shifts the gasoline curve slightly downwards after the midrange region. Figure 3 compares the distillation curves of G, E10, and NPA10 fuel blends. The Figure shows that ethanol causes a significant change in the distillation curve, while NPA has only a minor effect.

Ethanol causes a significant downward shift in the gasoline distillation curve due to the formation of an azeotrope between ethanol and some hydrocarbons in gasoline. This azeotrope has a lower boiling range than the constituents of gasoline. Figure 4 shows the effect of NPA on the values of T10 and T50 which are almost unchanged.

Calculating the area under the distillation curve can help in demonstrating any changes happened to the curve. Figure 5 demonstrates that NPA with different concentrations hardly affects the area under the distillation curve while ethanol has decreased the area significantly.

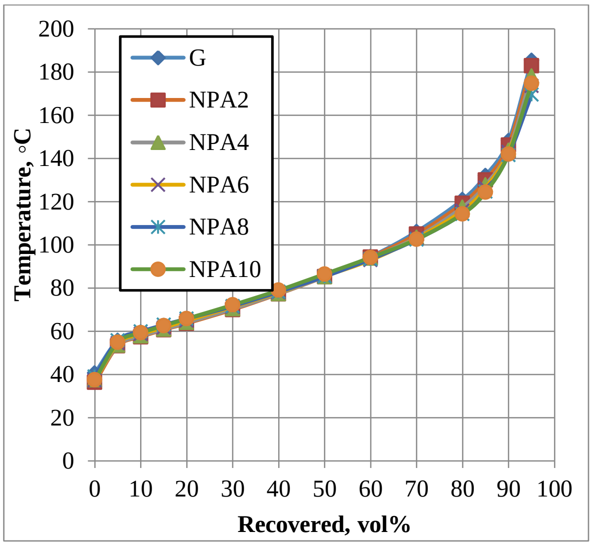

Figure 2: The effect of NPA addition on the distillation curve of gasoline.

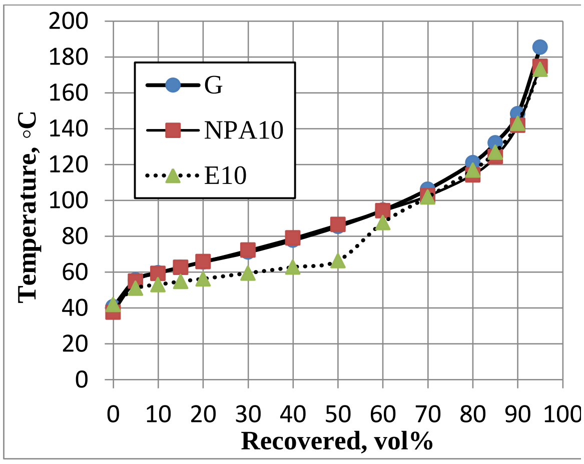

Figure 3: The effect of ethanol and NPA addition on the distillation curve of gasoline.

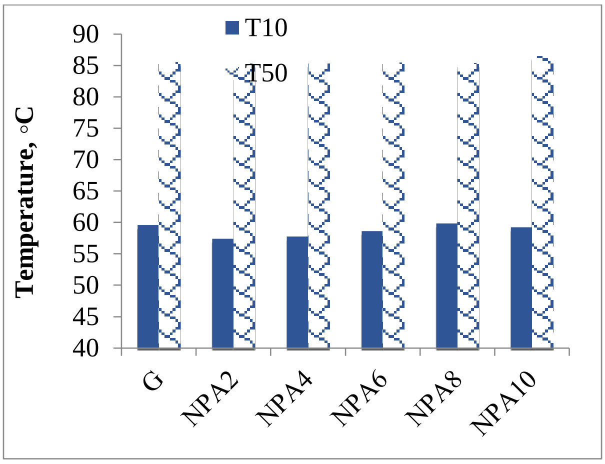

Figure 4: The effect of NPA addition on the T10 & T50 of gasoline.

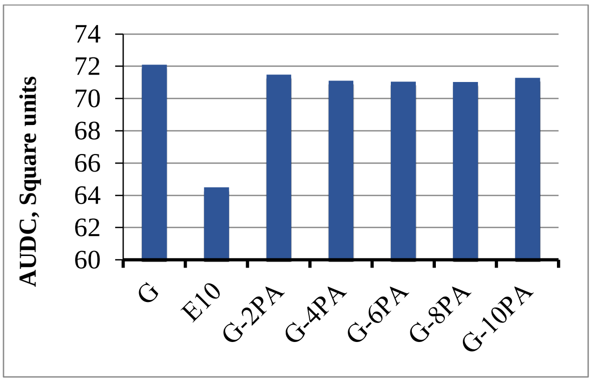

Figure 5: The effect of ethanol and NPA addition on the AUDC.

3.1.3. Driveability Index (DI)

One of the parameters used to measure the volatility of gasoline is the drivability index., and it is calculated using the fuel's distillation curve according to ASTM-D4814. It is a measure of the engine's drivability, and ASTM-D4814 has established limits for the drivability index between 375 and 610 °C. The DI values of NPA blends are within the specified limits. Figure 6 shows that DI decreases with the addition of low concentrations of NPA and rises again with the addition of high concentrations of NPA.

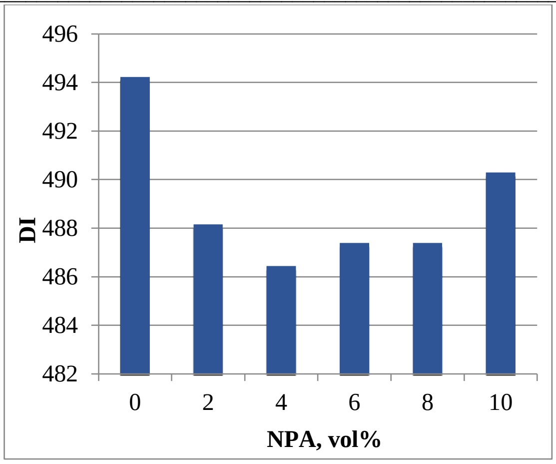

Figure 6: The effect of NPA addition on the deriveability index (DI) of gasoline.

3.1.4. Temperature of vapor liquid ratio of 20

Merely regulating the vapor pressure of gasoline is inadequate for managing its vaporization. Controlling the temperature at which the ratio of vapor to liquid equals 20 (T(V/L=20)) is important as it is another property that expresses the volatility of gasoline. Regulating this temperature is crucial in reducing the probability of vapor lock formation in the engine's fuel path. The fuel's tendency to form vapor lock increases as T(V/L=20) decreases, and vice versa. The standard limits for the temperature at which V/L=20 is typically set within the range of 35-60°C (95-140°F). Since T(V/L=20) is specified as a minimum temperature, any additive that raises this value is of benefit in meeting the standard. As shown in Figure 7, the T(V/L=20) decreases with the addition of low concentrations of NPA and rises again with the addition of high concentrations of NPA The obtained values exceed the minimum values specified for V/L=20.

3.2. Density

Density is a key parameter in controlling the quantity of fuel that enters the engine's combustion chamber. The density of gasoline can have an impact on its performance in engines in a few different ways. One of the main ways is through its effect on the fuel-air mixture that is used for combustion in the engine. The fuel-air mixture needs to be carefully controlled to ensure proper combustion and efficient operation of the engine. If the density of the gasoline is too low, it can lead to a lean fuel-air mixture, which means there is not enough fuel relative to the amount of air in the mixture. This can cause the engine to run hot and potentially damage it. On the other hand, if the density of the gasoline is too high (i.e., the gasoline is more dense than expected), it can lead to a rich fuel-air mixture, which means there is too much fuel relative to the amount of air in the mixture. This can cause the engine to run inefficiently, waste fuel, and produce more emissions.

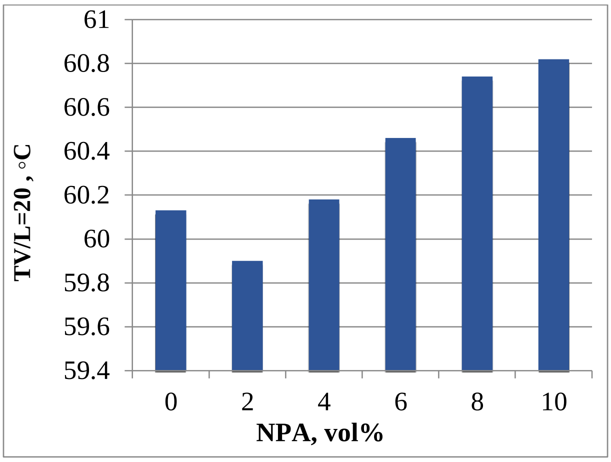

Figure 7: The effect of NPA addition on the TV/L=20 of gasoline.

Besides affecting the fuel-air mixture, the density of gasoline can also impact the amount of energy that is released during combustion. Gasoline with a higher density will contain more potential energy per unit volume than gasoline with a lower density. This means that, all else being equal, a car running on denser gasoline could potentially achieve slightly better fuel economy and performance than a car running on less dense gasoline. Typically, gasoline formulations have specific gravities ranging from 0.70 to 0.78 at 15.6°C. Table 5 shows that addition of NPA to gasoline causes a small increase in the density of gasoline. 10 % addition of NPA increases the density from 0.7208 to0.7465, g / cm3.

3.3. Oxidation stability

The oxidation stability of gasoline refers to its ability to resist the formation of harmful deposits and gum that result from exposure to oxygen over time. This property is important because the build-up of deposits can cause engine problems such as reduced fuel efficiency and increased emissions. Therefore, gasoline with higher oxidation stability is generally considered to be of higher quality. Table 3 comprises the values of the oxidation stability for some samples which show that NPA has no effect on the oxidation stability of gasoline.

3.4. Calorific value

Calorific value of a substance represents the amount of energy released when the substance is oxidized in presence of air or oxygen. The calorific value of gasoline can vary somewhat depending on the constituents of gasoline and their chemical composition, but a typical value is around 44000 (KJ/kg). The higher the hydrogen-carbon ratio of a compound, the greater its calorific value. Among compounds with the same number of carbon atoms, paraffins have been found to have the highest calorific value, followed by naphthenes, then aromatics [39]. Fuel with a high H/C ratio releases more energy per unit of carbon during combustion, which means it is more energy efficient. The presented study showed that oxygenates have a negative impact on the calorific value of gasoline due to their low hydrogen-carbon ratios. Table 3 presents calorific values of the fuel blends tested. Figure 7 illustrates the decrease in calorific value resulting from the addition of NPA. When comparing the calorific values of E10 and NPA10, it was observed that while the calorific value of E10 decreased from 44140 to 44029 KJ/Kg, the calorific value of NPA10 decreased from 44140 to 43888 KJ/Kg. This decrease can be attributed to the fact that ethanol has a higher hydrogen-carbon ratio than NPA.

3.5. Comparison between ethanol and NPA

Figure 9 provides a straightforward comparison between ethanol and NPA. The graph shows that ethanol leads to a significant increase in the vapor pressure of gasoline, while NPA causes a slight decrease in vapor pressure. It was found that addition of 10% n-propyl acetate into gasoline results in a reduction of approximately 2.3 kPa in vapor pressure while the addition of 10% ethanol increases the vapor pressure by around 5 kPa.

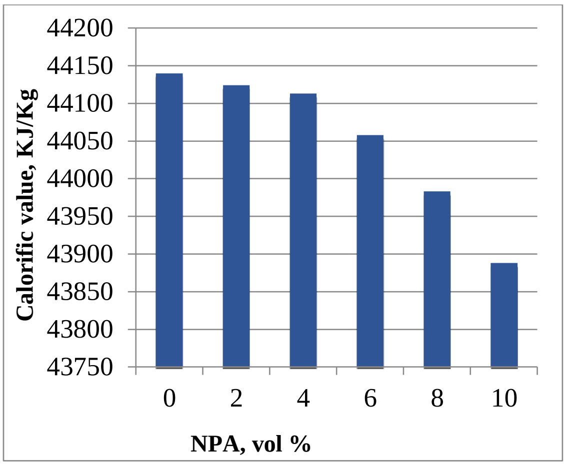

Figure 8: the effect of NPA addition on the calorific value of gasoline.

Ethanol also causes a significant decrease in T50, while NPA does not change T50. Additionally, ethanol leads to a significant decrease in T(v/l=20), whereas NPA causes a slight increase in T(v/l=20). Also, the Figure shows the decrease in calorific value caused by NPA which is in line with the expectation that NPA, with its lower hydrogen-carbon ratio compared to ethanol, would result in a greater reduction in calorific value.

4. Conclusions

- Addition of NPA to gasoline hardly affects the distillation curve of gasoline as the values of T10 and T50 are almost unchanged.
- Addition of NPA to gasoline causes a slight decrease in vapor pressure of gasoline.
- Addition of NPA to gasoline slightly increases the fuel density.
- Addition of NPA to gasoline does not affect the oxidation stability.
- Addition of NPA to gasoline decreases the calorific value.
- The results obtained highlight the importance of further studying the impact of NPA on the characteristics of gasoline.

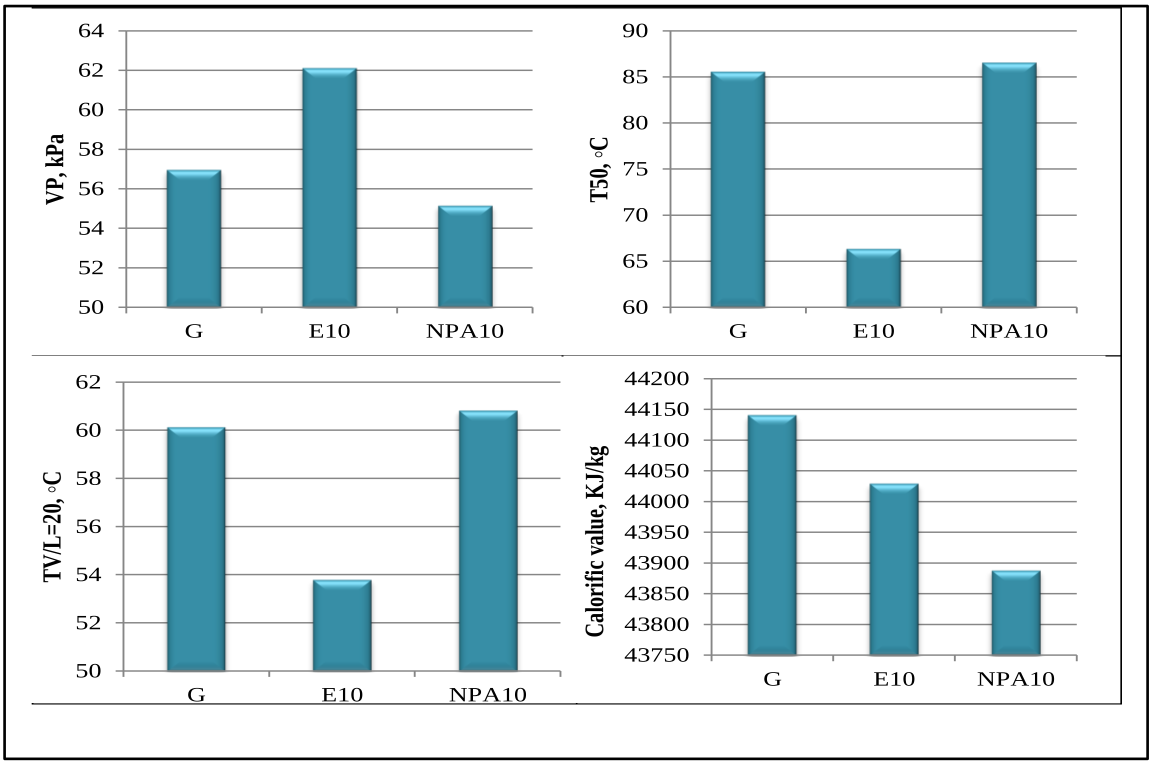

Figure 9: A comparison between ethanol and NPA addition on some properties of gasoline (G)

5. Conflicts of interest

"There are no conflicts to declare"

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Test	Standard Test Method		n-Propyl acetate	Gasoline	NPA2	NPA4	NPA6	NPA8	NPA10	E10
Density at 15.56 ^{o}C, g / cm^{3}	ASTM D - 4052		0.8885	0.7208	0.7225	0.7236	0.7293	0.7369	0.7465	0.7322
Specific gravity			0.8894	0.7215	0.7232	0.7243	0.7300	0.7376	0.7472	0.7330
^{o}API			27.6	64.62	64.2	63.87	62.34	60.33	57.88	61.55
Kinematic viscosity at 30^{o}C,cSt	ASTM D - 445		0.4231	0.2225	0.2279	0.2357	0.2417	0.2478	0.2711	0.2779
Flash point, ^{o}C	ASTM D – 56		———	< -20	< -20	< -20	< -20	< -20	< -20	< -20
Fire point, ^{o}C			———	< -20	< -20	< -20	< -20	< -20	< -20	< -20
Heating value (calorific value) ,KJ/Kg	Gross	ASTM D – 240	———	47334	47310	47294	47214	47114	46984	47165
	Net		———	44140	44124	44113	44058	43983	43888	44029
Water content, ppm	ASTM D – 6304		6365.19	191.71	220.12	268.92	431.28	476.76	575.61	656.1
Sulfur content , ppm	ASTM D – 4294		———	145.4	152.3	155.3	145.5	130.1	133.3	179.6
Ash content , wt %	ASTM D – 482		———	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Oxidation stability, min	ASTM D- 7525		———	>350	———	———	———	———	>350	>350

Table 3: Physicochemical properties of the fuel blends.