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Production of Premium Motor Spirit (PMS) additive from acetone and D-limonene

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Abstract

A PMS additive containing acetone, D-limonene and a synthetic two stroke oil was produced. This additive improves the efficiency of fuel it is used in and also serves as an injector cleanser in engines due to the presence of D-limonene. This product prevents the destruction of parts of engine (metal parts and rubbers) that occurs due to ethanol softening. This invention also eradicates the chances of water collection and phase separation that is present in ethanol use. ASTM test analysis revealed that a sample of our prototype has a cloud point of 34°F, Kinematic viscosity of 4.8 mm^2/s, Carbon residue of 0.2 and Research Octane number (RON) of 89. Manual test was also carried out to show the duration our PMS blended mixture which was 305 minutes and it lasts longer than pure PMS bought at a filling station which was 282 minutes.

Keywords: PMS additives; Injector cleaner; Emission reduction

1. Introduction

Fuel additive aids in maximizing fuel efficiency. It also prevents rough idling, weak acceleration and stalling of engines as well as enhances overall engine performance and thus keeping the engines running void of impurities [1]. With considerable increase in vehicle manufacturing globally the tendency of complications of unsustainable fuel consumption and environmental pollution is unavoidable [2]. Meanwhile, there is increasing notice in additives production which could curtail engine emissions. Bio-ethanol is among the PMS additives in use around the world to complement PMS although it is also seen as a viable energy source produced from sugarcane, cassava or corn [3]. Bio-ethanol as a fuel additive curbs greenhouse emissions and global warming [3]. Ethanol's according to possess [4] latent heat of vaporization and octane number as well as oxygen number higher than that of PMS which makes it a key raw material in the production of fuel additives. The benefits of fuel additives cannot be debated hence, they remain a popular product at consumer PMS stations due to the following advantages; the ability to increase the octane rating of fuel. When added to the fuel tank they improve engine performance aids acceleration and overall engine efficiency [5]. Fuel additives actively target reduction in corrosion of engine parts; they act as lubricants and prevent combustion deposits from building up. Fuel additives cleanse up fuel injection in older vehicles, fuel additives reduces carbon buildup in the engine valves [1]. The presence of high octane ratings in these additives represents cleaner burning of fuel and better engine performance which in turn results to better mileage.

In the general production of premium motor spirit additives, the major challenge has been the presence of ethanol which is the major raw material needed in the production process. The presence of ethanol in fuel additives is harmful to the engine as it pulls water into the petrol wherever it is present. And a mixture of ethanol and water at the base in turn causes serious damage to the engine. This challenge led to the production of a new brand of PMS additive which does not contain ethanol. Ethanol was completely replaced with acetone , D-limonene and synthetic two stroke oil in this new PMS additive because acetone possesses desirable properties such as high octane number and good flash point that rivals' ethanol also acetone is not hygroscopic like ethanol. Acetone boosts the octane level of fuels where it is used. It is also cheap and easy to purchase in global market as it is formed in the bodies of living animals [6,7,8]. D-limonene obtained from the peels of citrus fruits is very active in injector cleaning. D-limonene is used as a dispersant and also has good octane boosting abilities as it is combustible and has been considered as a biofuel. It also increases the stability of PMS. It is a colorless liquid and noted as the major component gotten from the oil of citrus fruits peels. D-limonene is obtained from fruits through centrifugal separation or steam distillation; it also provides advantages such as increasing volumetric efficiency, engine knock suppression, engine performance enhancement, more complete burning and emission reduction [9,10]. The synthetic two stroke oil is easily available since it is commonly used in machines like mopeds, chainsaws and lawn mowers. This oil is helpful in increasing the lubrication of the engine [11].

These additives may be added to PMS at the refinery, in the fuel distribution system, and by the end user at home.

2. Materials and method

The materials used for the production of this additive are acetone, a high quality synthetic two stroke oil and D-limonene (gotten as a by-product of orange peel), iso-propanol. There properties are given in Table 1 and 2 [9].

2.1. Method

2.1.1. Extraction of D-limonene from citrus peel

Of the two methods available for the extraction of D-limonene from the peel of citrus peel, distillation process was adopted be-

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Table 1: Properties of acetone.

Chemical Formula	(C_3H_6O)
Molar Mass	58.080 g/mol
Appearance	Colourless liquid
Density	0.7842g/cm^3
Melting Point	-94.7°C (178.5 K)
Boiling Point	56.05°C (329.20 K)
Solubility in water	Miscible
Vapour Pressure	30.6 kPa (25°C)
Acidity (Pk$_a$)	19.16 (H_2O)
Refractive Index (n_D)	1.3588 (V_D = 54.46)
Viscosity	0.295 mPa.s (25°C)
Heat Capacity (C)	125.45 J/(mol·K)
Flash Point	-20°C
Auto Ignition Temperature	465°C

Table 2: Properties of D-limonene.

Chemical Formula	$C_{10}H_6$
Molar mass	136.238 g.mol^{-1}
Density	0.8411 g/cm^3
Melting Point	-74.35°C (198.80 K)
Boiling Point	176°C (449 K)
Solubility in water	Insoluble
Refractive Index	1.4727
Standard enthalpy of combustion	-6.128 MJ mol^{-1}
Flash Point	50°C
Auto ignition temperature	237°C

cause of its effectiveness in separation. Limonene was obtained from citrus plants after distillation and treatment to avoid formation of gums. limonene is blend able with conventional PMS.

A supply of citrus plant peel preferably orange peel (40 pieces of orange was used in this process). The orange is then grated by carefully removing the first layer of its skin because a high amount of D-limonene is found here. The grated peel was mixed with iso-propanol in a round bottom flask for distillation and the mixture was distilled at temperature ranging from 346°F (174°C) to 382°F (194°C) for about 5 hours. The distillate was collected through a round bottom flask (the distillate contains a mixture of iso-propanol and D-limonene). The distillate was passed through a rotary evaporator in order to separate the D-limonene from the iso-propanol. D-limonene is left in the evaporation flask present in the rotary evaporator. Antioxidant was added to the distilled limonene in order to prevent gum formation.

In the first experiment for distillation, water was used as the solvent in order to extract the D-limonene. After the rotary evaporating process however, the distillate gotten was totally evaporated due to the high boiling point of water. Iso-propanol was then chosen as the ideal solvent to use for this distillation process as it has a boiling point of 53°C.

A ring support is clamped to the retort stand and the distilling flask contains the liquid that is heated from underneath by a heating mantle. A thermometer sits at the neck of the flask to allow monitoring of the vapour temperature. The thermometer allows the temperature of the vapour to be controlled to correspond with the boiling point of the D-limonene.

The orange peels was transferred to the distillation flask and mixed with iso-propanol in order to facilitate extraction of the D-limonene. The mixture was heated to the boiling point of limonene and kept between 174°C to 194°C. The liquid evaporates forming a vapour. The vapour is then cooled by the tubes in the condenser at a lower temperature. The cooled vapour condenses, forming a

Figure 1: D- Limonene sample.

distillate that drops into the Receiving Flask (Conical Flask). The distillate is a mixture of iso-propenol and D-limonene. The resultant limonene product obtained within temperature range of 174°C to 194°C showed a purified D-limonene whose purity level is about 97.8 per cent according to [12].

2.1.2. Separation of solvents

For the separation of the mixture, rotary evaporator (rotavaps) was used. The rotary evaporator was used to remove solvents from mixtures.

The distillate was transferred to a round bottom flask (evaporation flask). Distilled water was poured into the water bath. The vacuum system, the condenser and rotating motor units were all connected to a power supply. The flask was attached to main part of the rotavaps and secured with a clip and then lowered into the water bath. The rotating motor is switched on and rotates at a specific maintained speed. The heat for the water bath turned on as the water bath begins to bubble, the distillate begins to heat up. Isopropanol (which is the solvent with the lower boiling point) evaporates and then condenses in the condensate-collection flask while the D-limonene remains in the evaporation flask as the residue after the heating process.

2.1.3. Processing of D-limonene to preclude gum formation

Limonene with a cyclic olefinic compound is avoided by the petroleum industry due to the presence of olefinic double bonds in the product. This is because olefins are gum producing compounds and residual gums in fuels are to be avoided. However, limonene is processed as discussed earlier; subsequent gum formation was precluded by putting the D-limonene in a vessel in which antioxidant is injected into in a nitrogen stream. A number of antioxidants can be used but here the antioxidant used is phenylenediamenes [13].

The D-limonene product (Fig. 1) comprises of colourless distilled limonene, having a purity of at least 95percent, water level not greater than 0.1percent, an octane number of not less than 90 and absence of olefinic double bonds that enable gum formation [14]. It also includes a minor amount of antioxidant.

2.1.4. Mixture of the solvents and administration

The mixture of the acetone, D-limonene and two stroke cycle oil was done in a ratio of 2:1:1. The mixing was done with a 50 ml measuring cylinder, a reagent bottle and a spatula. Twenty ml of acetone was mixed with 10 ml of D-limonene and 10 ml of the two stroke cycle oil. The result was a lemon coloured liquid with distinctive citrus smell (Fig. 2). As a basic and safe approximation, it is recommended that 89 ml of the additive should be used for every 10 liters of PMS. Using lesser amount of the additive will only dilute the PMS without improving the car's performance. It is recommended to add additives into the tank when the PMS is almost exhausted (nearly empty fuel tanks). After pouring the additive,

Figure 2: PMS addictive from acetone D-limonene and two stroke cycle oil.

Table 3: Comparison of product properties and the standard ASTM specification.

	New product	Standard value
Carbon residue, wt.% D-4530	0.22	Max 0.2 – 0.3
Specific gravity	0.88	-
Kinematic viscosity, mm^2/s	2.1	1.9 – 6.0
Cetane Index, % D-613	52	48.0 – 55.0
Flash point (Closed cup), °F D-56	154	Min 131
Density at 15°C D405, kg/m^3	742	Min 715 – 720 to Max 775 – 780
H, wt.%	11.3	Min 13.4
O, wt.%	30.2	-
Octane Number Research (R) D-2699	89	91 – 98
Lead content, g/gal D-7111	0.1	Max 1
Sulphur, wt.% D-4294	0.17	0.015 – 5
Phosphorus, wt.% D-3231	0.02	No Specifications
Magnesium wt. %D-7111	Nil	-
Mercaptan Sulphur, wt. % D-3227	0.001	Max 0.003
Cloud point	34	<50

the tank should be re-fuelled. Instead of immediately driving the car, it is recommended to let it idle for some few minutes.

3. Results and discussion

Several tests were carried out to determine the quality of the additive after production. The prototype produced was tested for conformance with certified American society for testing and materials (ASTM), and standard for refined petroleum products. Results are shown in Table 3 along with its ASTM test method and ASTM standard range of values. Table 4 shows the comparison result with colonial pipeline standards for such properties for 87-octane leaded gasoline. These tests were carried out at Sondrex Laboratory and Dave First Ltd.

The product produced was tested for other physical characteristics relevant to the global market in other to conform to the standard specification.

From Table 3, which is the comparison between the tests of our proposed prototype to established PMS standards, the PMS standards were met by the product. Our product blended well with commercial PMS at the end user as an aftermarket additive without causing unacceptable deviance from established standards. With the high flash point measurements of the product, it is noted that this product is less volatile than conventional PMS and therefore, it is will blend well with PMS or Diesel.

Table 4: Comparison of product result and 87-octane leaded gasoline.

	New product	87 Octane
Lead content, g/gal D-7111	0.1	Nil
Sulphur, wt.% D-4294	0.17	0.0003
Mercaptan Sulphur, wt. % D-3227	0.001	Nil
Octane Number Research (R) D-2699	89	

Figure 3: Elepaq gasoline generator.

The quality of many petroleum products is related to the amount of sulphur present. From Table 4 our prototype contains more sulphur than unleaded PMS. Our prototype also contains a high level of lead and Mercaptan sulphur which has an adverse effect on the engine system components..

Performance tests of the additive mixed with PMS to determine its operational reaction was also carried out using Elepaq gasoline generator (Fig. 3). Four liters of PMS was mixed with 18 ml of our additive according to the specification stated earlier. The blended PMS burned well in the generator with clean fumes.

Comparison of the difference in time taken before 4 liters of blended PMS and 4 liters of the pure PMS is shown in Table 5. Appliances like fan, bulb and a television set were switched on during the test for both.

Table 5: Duration of pure PMS and blended PMS.

	Duration
Pure PMS	282 minutes
PMS plus additive	305 minutes

From the obtained result, it shows that PMS blended with acetone and D-limonene according to our invention lasts longer than pure PMS sold at the filling stations.

4. Conclusion

PMS additive from acetone, D-limonene and two stoke synthetic oil was produced in the ratio of 2:1:1 for acetone, D-limonene and two stroke synthetic oil. the product was tested and compared with ASTM standards for kinematic viscosity, carbon residue, cloud point, density at 15°C, flash point, octane number and specific gravity. The cloud point result was 34°F in accordance with the standard of less 50°F, and the specific gravity came out at exactly 0.88. Kinematic viscosity was tested and the result was $4.8 mm^2/s$ which was within the standard range of $1.9 – 6.0\ mm^2/s$. The carbon residue gotten 0.22 was within the standard maximum range of 0.2 – 0.3. The Cetane index of 52 also falls within the ASTM range of 48 – 55. The flash point of 154 gotten from the test was more than the standard minimum of 131. Although, the research octane number of our additive 89 was lower than the ASTM range of 91 – 98.

The blended PMS lasted a significantly higher number of minutes (305) when compared to that of pure PMS (282) bought at a local filling station.

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