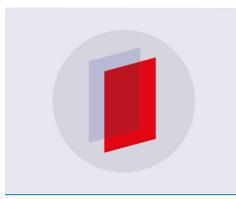
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FTIR Investigation of the Effect of Storage on Ogogoro-Gasoline Blend's Stability

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Abstract. Ethanol has wide application as spark ignition (SI) engine fuel and its usage comes as blend with gasoline or as sole fuel. Industrially produced anhydrous ethanol has been the type of ethanol used for this purpose. There has been conscious drive by governments and researchers over the years for a shift from environmentally detrimental energy sources to more environmentally friendly and renewable energy sources. Fourier-Transform Infrared (FTIR) spectrums were obtained from ogogoro in its pure state and when mixed with 90% by volume of gasoline before and after a year of storage. The spectrums obtained before and after storage were compared and the results showed that there was no significant change in their chemical compositions. The FTIR results and physical observation showed that the ogogoro and its blends were chemically and physically stable, confirming its suitability as fuel for spark ignition engines.

1. Introduction

Ethanol has been found to be a promising fuel, suitable for use by internal combustion engines. Internal combustion engines will remain major players in the automobile and related industries in the years to come [1, 2], due to increased demand to develop fuels to power them. Over the years it has been observed that the fuel from non-renewable sources are fast depleting and this has necessitated a shift from non-renewable energy sources to renewable sources [3,4]. It is worthy of note that with the growing world population, the demand for this limited resource will continue increase. As a result, other sources of fuel for these engines are required.

In recent years, there has been a conscious drive by the government and researchers to shift from toxic and environmentally detrimental energy sources to more sustainable and renewable energy sources [5-7]. World agreements such as the Kyoto Protocol [8], Paris agreement [9], etc. have all been reached and signed to ensure this goal is realised.

To reduce the contribution of greenhouse gases made by spark ignition engines, the use of ethanol or ethanol-gasoline blends seems to be the answer. Ethanol is obtained from renewable sources, it has better antiknock quality compared to gasoline and it gives more environmentally friendly by-products [10, 11]. The following qualities have made ethanol the future fuel for SI engine.

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While anhydrous ethanol is commercially used, there is limited literature on hydrated ethanol and the effect of its use as blend with gasoline, on the performance as fuel in SI engines. An experimental study by Uguru-Okorie et al. [12] has shown that a hydrated ethanol obtained from fermented palm tree sap, known as Ogogoro, could be used as fuel for SI engines when blended with gasoline.

Crudely produced ethanol (also known as ogogoro) blended with gasoline in an SI engine has been experimentally studied with results published, showing an improved engine performance in its 1 to 5% by volume blend with gasoline. The stability of this blend in storage overtime, has not been investigated and this finding led to the research on the FTIR investigation of the stability of Ogogoro-gasoline blend over time.

2. Production of Ethanol Locally

Ethanol is popularly produced in Nigeria from the sap of raffia palm and oil palm tree [13]. The sap obtained is further processed to a substance with higher ethanol content known as Ogogoro. The processing involves harvesting the sap of a raffia palm and oil palm tree and thereafter, it is left to ferment and this is done by leaving it in an enclosure for seven (7) days. The solution is subsequently heated up to steam and the steam is condensed to liquid whose distillate is consumed as locally produced alcohol known as Ogogoro [14, 15].

This locally produced ethanol (ogogoro) is known to have between 30-60% alcohol content [16-20] and it's consumption as drink is said to be harmful because of the unhygienic mode of production [14][21, 22] Ethanol is also produced from other biological components which are referred to as feedstock [23,24]. These feedstocks are classified into three major groups: simple sugar, starches and lignocellulosic biomass. The sources of raw materials in each of the groups are as follows: simple sugar: sugarcane, sugar beet and sorghum, starches: corn, wheat, potatoes [25] and cassava and lignocellulosic biomass: mix of lignocellulosic.

The extraction of ethanol from simple sugar raw materials starts with a milling process for sugar extraction which is later fermented. Subsequently, fermentation, distilling, rectification and finally dehydration processes take place [26,27]. For the starches group, which comprise the grains, it starts with the milling of the grain, which could be done in wet or dry condition. If the milling is done in wet condition, the starch in the grain is extracted and then fermented and if the milling is done in dry condition, a mash is formed by adding water to the product and it is then allowed to ferment. For the lignocellulosic group, a more complex technology compared to simple sugar and starches is employed for the production of ethanol. The process starts with pre-treatment, hydrolysis, fermentation and finally product separation.

2.1 Use of Ethanol-Gasoline Blends in SI engines

In recent years, ethanol-gasoline blends have been used as fuels in spark ignition engines with the "E" describing the percentage of ethanol by volume in the mixture. Examples are E5 denotes that the fuel contains 5% anhydrous ethanol and 95% gasoline by volume while E85 denotes that the fuel contains 85% anhydrous ethanol and 15% gasoline [3,4].Research has shown that more than 10% content of ethanol in ethanol-gasoline mixture as fuel in SI engines requires modification of such engine [28].

2.2 Performance of Ogogoro-Gasoline Blend

Anhydrous ethanol blended with gasoline has been widely used in spark ignition engines while the hydrous ethanol used as sole fuel is reported to have about 96% content of ethanol and about 4% of water by volume [28-31]. While ethanol used as blends with gasoline are industrially produced ethanol with high purity, there is no records of studies done with ogogoro (which is reported to contain between 30 to

60% ethanol by volume) mixed with gasoline, as fuel for spark ignition engines apart from the one carried out by Uguru-Okorie et. al. [12].

The investigation on the potential of the blends of ogogoro-gasoline as spark ignition engines fuel, was carried out in a four-stroke, single cylinder, SI engine with between 1 to 5% by volume ogogoro content in gasoline fuel. Pure regular gasoline was the base fuel and was assigned E0 while E1, E3 and E5 were gasoline fuels with 1, 3 and 5% content of ogogoro by volume. The study showed improved performance of the blends over pure gasoline while the best engine performance was with gasoline with 3% by volume content of ogogoro. Results obtained are shown in figures (1) and (2).

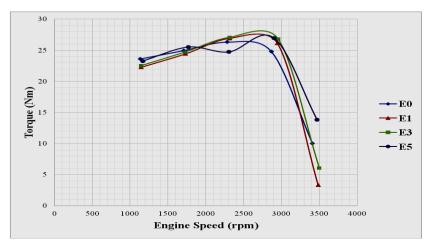


Fig. 1 Engine Torque at Varying Speeds [12]

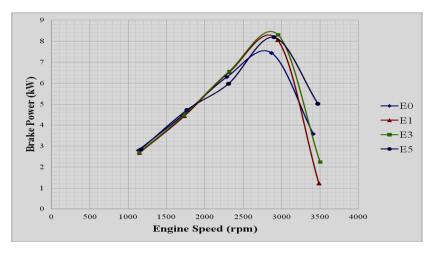


Fig. 2 Brake Power at varying Speeds [12]

3. Methodology

This research is based on Fourier-Transform Infrared (FTIR) Spectroscopy test for the stability of ogogoro-gasoline blend as fuel for spark ignition engine, over a period of fourteen (14) months. The stability of the fuels was investigated by the study of functional groups present in the pure fuels (gasoline and ogogoro), as well as their blends before and after storage. The following steps were taken in the investigation: -

a. FTIR spectrum from ogogoro (obtained from palm wine source) was obtained before storage.

- b. FTIR spectrum from unleaded gasoline was obtained.
- c. FTIR spectrum of ogogoro and gasoline blend in the proportion of 10 and 90% by volume respectively was obtained.
- d. FTIR spectrum from ogogoro, in storage, for fourteen (14) months, in a thermo-set container, was obtained.
- e. FTIR spectrum of ogogoro and gasoline blend in the proportion of 10 and 90% by volume respectively stored for fourteen months, in a thermo-set container, was obtained.
- f. FTIR spectrums obtained from pure gasoline and ogogoro-gasoline blend were compared.
- g. FTIR spectrums obtained from ogogoro-gasoline blend and old ogogoro-gasoline blend in storage for 14 months were compared.
- h. The FTIR spectrums from pure ogogoro before storage and after fourteen (14) months storage were compared to determine if there were variations in the functional groups.
- i. FTIR spectrums obtained from pure gasoline, ogogoro-gasoline blend and old ogogoro-gasoline blend were compared.

4. Analysis of FTIR Spectrum of Gasoline Fuel

The following functional groups were observed in the spectrum for pure unleaded gasoline seen in figure (3): terminal (vinyl) C-H stretch at 3026.31cm-1 at 97.73%, methyl C-H asymmetric or symmetric stretch at 2956.87cm-1 at 79.14% transmittance, methylene C-H asymmetric or symmetric stretch at 2924.01cm-1 at 80.40% transmittance, methylene (CH2)n rocking at 731.02cm-1 at 85.18% transmittance, aromatic ring stretch at 1458.18cm-1 at 86.54% transmittance, mono-substitution (phenyl) at 696.30cm-1 at 88.87% transmittance, meta-di-sub benzene at 881.47cm-1 at 97.58% transmittance [32-34].

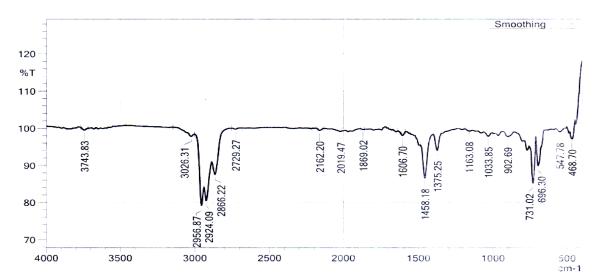
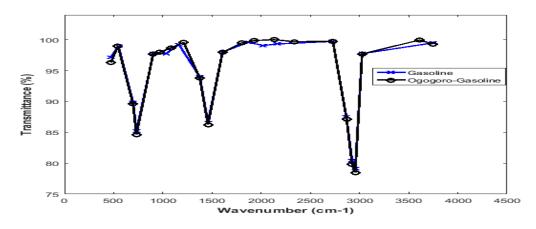


Fig. 3 FTIR Spectrum for Pure Gasoline

4.1 FTIR Comparison of Pure Gasoline and Ogogoro-Gasoline blend

The FTIR spectrums for gasoline and ogogoro-gasoline blend were compared as shown in figures (4) and (5). The FTIR data obtained from pure gasoline was similar to that obtained from the FTIR data of ogogoro-gasoline blend, when compared. With 10% by volume of ogogoro in gasoline, the alcohol content in the ogogoro-gasoline blend was visible on the FTIR spectrum as shown in figure (9).





4.2 Storage Effect on Ogogoro and Ogogoro-Gasoline Blend

The storage effects on pure ogogoro and a blend of ogogoro with gasoline were investigated with the FTIR spectrometer to determine if long storage gave rise to degradation.

4.2.1 Storage Effect on the FTIR Spectrum of Ogogoro

The strong intensity of alcohol in both the fresh and old ogogoro in storage were maintained at transmittance between 57.96 to 60.38%; between the wavenumbers of 3200-3400 cm-1 and also other intensities at other wavenumber in the FTIR spectrums for the new and old ethanol in storage remained the same as shown in figures (5) and (6). The results from the comparison of the FTIR data obtained from the fresh and old ogogoro in storage and physical observation show that there was no noticeable change in both chemical and physical composition of ogogoro after over fourteen (14) months in storage. The peaks from the spectrums were compared with no significant difference as shown in figure (7).

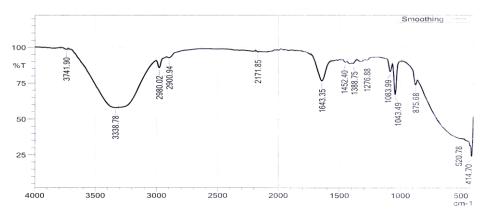


Fig. 5 FTIR Spectrum for Ogogoro before storage

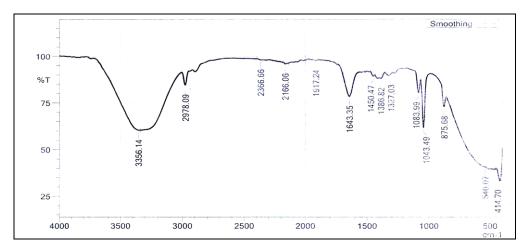


Fig. 6 FTIR Spectrum for Ogogoro after Storage (14 months)

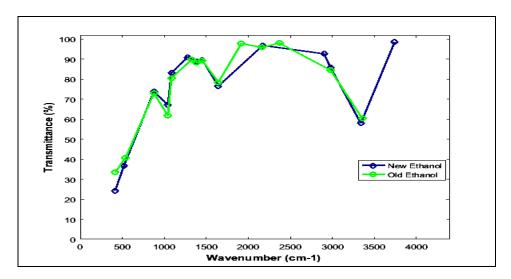


Fig. 7 FTIR Spectrum Peaks of Old and New Ogogoro

4.2.2 Storage Effect on Ogogoro-Gasoline Blend

The FTIR spectrums for the fresh ogogoro-gasoline blend and the old ogogoro-gasoline blend in storage for fourteen (14) months, when compared, showed very similar structures with slight variations in the intensities of the functional groups present, as seen in figures (8) to (10). The graph for fresh ogorogo-gasoline is represented with "New Etha-Gas" while ogogoro-gasoline in storage is represented with "Old Etha-Gas".

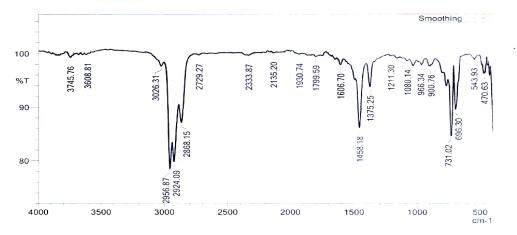


Fig. 8 FTIR Spectrum for Ogogoro–Gasoline Blend

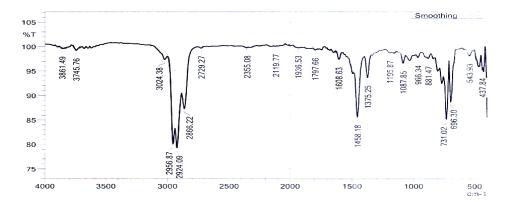


Fig. 9 FTIR Spectrum for Ogogoro–Gasoline Blend in Storage (14 months)

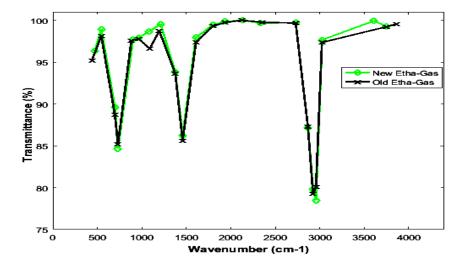


Fig. 10 FTIR Spectrum Peaks of Old and New Ogogoro-Gasoline Blends

5. Conclusions

The aim of the research work was to investigate the effect of prolonged storage of ogogoro-gasoline blend on its chemical stability, which was investigated using an FTIR spectrometer. The FTIR spectrums of the fuels were obtained and analyzed, before and after storage in its pure and blended states. At the end of the investigation, the following findings were made:

- (i) FTIR spectrum obtained, showed negligible trace of alcohol in 10% ogogoro-90% gasoline blend, when compared with pure gasoline.
- (ii) The FTIR spectra obtained from the fresh ogogoro and ogogoro in storage for 14 months and physical observation showed no change in both chemical and physical composition. The result proves that ogogoro is chemically and physically stable.
- (iii) FTIR spectrum obtained from new ogogoro-gasoline blend when compared with the spectrum obtained from ogogoro-gasoline in storage (14 months), showed no significant change in the structure of the fuels.
- (iv) The findings show that ogogoro-gasoline is a stable fuel and is resistant to degradation in storage.
- (v) This observation rules out the need for preservatives to maintain the stability of ogogorogasoline blend in storage and this makes the use of this fuel promising for SI engines.

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