Determination of Alkali and Alkaline-earth Metal Content of Bio-diesel Produced from Palm Oil, Palm Kernel Oil and Neem Seed Oil Feed stocks

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ABSTRACT

Standards are prescribed for fatty acid methyl esters (FAME) used as biodiesel fuels. For its adequate use, biodiesel must conform to these strict standards. The determination of Na, K, Mg and Ca is part of biodiesel characterization of pure biodiesel B100 or blends with petroleum diesel (B2, B5 and B10). Regulations by means of standard methods such as EN 14108, EN 14109, EN 14538 and ASTM D6751 establish a limit of 5 mg/kg as the maximum allowed concentration for Na plus K or Ca plus Mg. Alkali (Na + K) and alkaline earth (Ca + Mg) metal content of biodiesel samples produced from different feed stocks such as palm, palm kernel and neem seed oils was determined using the direct solvent method and a Buck 210VGP Atomic Absorption Spectrophotometer. The mean concentrations of Na, K, Mg and Ca are 19.1, 5.17, 1.8 and 0.00 mg/kg for palm biodiesel, 49.15, 73.2, 1.56 and 0.24 mg/kg for palm kernel biodiesel and 0.26, 111.3, 1.49 and 0.2 mg/kg for neem seed biodiesel respectively. The concentration for Ca plus Mg in all the biodiesel samples was within the maximum limit of 5 mg/kg. This however is not so for Na plus K as its concentration in all the samples exceeded this limit. Analysis of the fuel properties of the biodiesel produced from these feed stocks agreed closely with ASTM D 6751 .

***Keywords**: Biodiesel characterization, Alkali and Alkaline earth metals, AAS, direct solvent method.*

1. INTRODUCTION

The fluctuating price and environmental impacts associated with petroleum-based fuels has led to the exploration of a renewable alternative fuel – Biodiesel. It is considered a renewable energy source because it is obtained from biomass feedstock. It can be substituted for petroleum-based diesel fuel (petro-diesel) in virtually any standard unmodified diesel engine [1, 2]. Pure biodiesel or biodiesel blended with petroleum diesel can be used to fuel diesel vehicles, providing energy security, emissions and safety benefits. The ASTM D6751-08 specification, defines biodiesel as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. Pure, neat biodiesel is designated B100 [3].

Emissions from combustion of this biofuel are essentially free of aromatic compounds, heavy metals such as Cd, Co, Cu, Pb, V and Ni and other pollutants such as NO_x and SO_x that affect the air quality [4]. These among others form the basis for its consideration as an alternative energy source to petro-diesel.

Na and K hydroxides or methylates are used as a catalyst for biodiesel production. Alkali metals in the biodiesel originate from the catalyst used for the biodiesel production. Na and K are usually present as soaps which are not fully removed in the wash. Soaps can lead to filter blockages and adhesions of injection pumps and nozzles. Another important aspect is ash formation: in particular Na accumulates on the surface of particle filters and oxidation catalysts, thereby reducing the efficiency and service life of the systems. Suitable process conditions allow the alkalimetal content to be reduced to concentrations below the determination limit of the specified test method [5].

Alkaline earth metals, Ca and Mg enter the biodiesel when using tap water for the water wash; Ca and Mg soaps are formed by reaction with free fatty acids.Soaps of alkaline earth metals are more voluminous than alkali metal soaps and can lead to filter blockage and adhesion of injection pumps. The entry of alkaline earth metals into biodiesel can be prevented by using soft water (condensate, demineralised water) [5].

Since the presence of Na, K, Ca and Mg in biodiesel are undesirable even at lower concentrations, a consistent quality assurance program is necessary to avoid performance issues in vehicle engines and to ensure sustainable growth of biodiesel production. The determination of the levels of these elemental contaminants in bio-fuel is necessary to evaluate fuel quality, to see their effect on auto engines, and to control environmental pollution.

Maximum limits for these elemental contaminants are given in biodiesel specifications as shown in Table 1. The objectives of this study therefore are to determine the concentrations of Na, K, Ca and Mg in the biodiesel samples and consequently their quality by comparison with set limits.

Table 1 Biodiesel specifications adopted in USA, Brazil and EU [6]

Quality Parameter	Limits			
	Units	USA ASTM D6751/2003	EU EN/14214/2003	Brazil ANP 07/2008
Na + K	mg/kg	5 max	5 max	5 max
Ca + Mg	mg/kg	5 max	5 max	5 max

2. MATERIALS AND METHOD

2.1 Sample Collection

Biodiesel samples used in this study were produced in the Chemical Analysis Laboratory of Projects Development Institute (PRODA) Enugu. They were stored in 2-liter plastic containers and kept in a cool dry place prior to further analysis.

2.2 Sample Pre-treatment

The determination of Na + K and Ca + Mg content in the biodiesel samples is consistent with prescribed test methods using Atomic Absorption Spectroscopy (AAS): EN 14108-03, EN 14109-03, NBR 15554-08, NBR 15555-08, UOP 391 for Na + K and ASTM D4951-09, EN 14107-03, NBR 15556-08 for Ca + Mg [6].The direct solvent method was used in these determinations using a 1: 10 (mass/volume) dilution of the sample with an organic solvent. 5 grams of each biodiesel sample was diluted with Xylene solvent to 50 cm^3. These diluted solutions were directly aspirated into a Buck 210VGP Atomic absorption spectrophotometer. The results were determined in duplicates.

2.3 A.A.S Determination of Alkali and Alkaline earth metals.

Analytical grade reagents and distilled water were used in preparing all solutions. Stock solutions containing 1000 mg/kg of the analyses were prepared from Chloride salts of Na, K, Ca and Mg. Working standard solutions were prepared by appropriate dilutions of the stock solutions. Blank determinations were run by using the same reagents inequal quantities as described in the analysis procedure. The Na, K, Ca and Mg content of each solubilized sample was determined with a Buck 210VGPAtomic Absorption Spectrophotometer with an air-acetylene flame. Metal contents were calculated by comparison with the standard curves of the respective metals. Hollow cathode lamps having resonance lines at 589.0, 703.0, 422.7, 202.6nanometers, were used as radiation sources for the determination of Na, K, Ca and Mg respectively. Lamp intensity and band pass were used according to the manufacturer's recommendations. Acetylene and air flow rates were 5 and 20 L min^{-1}, respectively, for all the elements.

2.4 Physicochemical Analysis

Further characterization of the biodiesel samples was done to determine some fuel quality parameters as specific gravity, kinematic viscosity, flash point, cloud point, pour point, acid value, percentage moisture, percentage yield and colour. This was done with a view to comparing them with ASTM D 6751 and ASTM D975 standards for biodiesel and diesel fuels respectively.

The specific gravity of the samples was determined by pycnometer using EN ISO 3675, kinematic viscosity using a Cannon -Fenske Capillary Visco meter tube according to ASTM D445, flash point by Pensky– Martens Flash apparatus by ASTM D93 method, cloud point and pour point by cloud and pour point apparatus by ASTM D 2500 method. Acid value was determined by titrimetry and moisture content by the oven dry method. The colour was determined by sensory evaluation. Analytical-grade reagents were used for all the analysis carried out.

2.5 Data Analysis

The IBM-SPSS 20.0 statistical software was used in the data analysis. Standard deviations for the measured concentrations of these metals were calculated and are based on measurements in duplicate.

3. RESULTS AND DISCUSSION

3.1 Na, K, Ca and Mg Content of Biodiesel Samples

The results obtained for Na, K, Ca and Mg content in all the biodiesel samples as presented in Table 2 are presented as mean ± standard deviation.

Table 2 Na, K, Ca and Mg Content of Biodiesel Samples (mg/kg)

S/N	Sample	Na	K	Ca	Mg
1	Palm kernel biodiesel	49.15±0.07	73.2±1.98	0.24 ±0.01	1.56 ±0.49
2	Neem biodiesel	0.26±0.08	111.3±0.1	0.2 ±0.04	1.49 ±0.13
3	Palm biodiesel	19.1±0.14	5.17 ±0.08	0.00	1.81 ± 0.12

The relative abundance of these elemental contaminants in the biodiesel samples follows the order K>Na>Mg>Ca. There is a greater abundance of the alkali metals Na and K than the alkaline-earth metals Ca and Mg in the samples. Palm kernel biodiesel had the highest level of Na content at 49.15 mg/kg while the Neem biodiesel had the lowest value at 0.26 mg/kg. Biodiesel from Neem oil feedstock however had the highest value of K at 111.3 mg/kg while Palm biodiesel had the least at 5.17 mg/kg. The highest value for Ca was observed in Palm kernel biodiesel at 0.24 mg/kg, while in Palm biodiesel, its value was below the detection limit of the instrument. This low level of occurrence was also observed for Mg as its highest value is observed in Palm biodiesel at 1.81 mg/kg and the lowest value of 1.49 mg/kg is observed in Neem biodiesel.

3.2 Na + K and Ca + Mg Content of Biodiesel Samples

The alkali metals, Na + K and alkaline-earth metals Ca + Mg contents of the biodiesel samples were calculated from the results and compared with standard biodiesel specifications. These are as shown in Table 3.

Table 3 Comparison of Na + K and Ca + Mg Content of Samples with Biodiesel Specifications

Quality Parameter	Units	Biodiesel Sample			Limits		
		Palm Kernel	Neem	Palm	USA ASTM D6751/2003	EU EN/14214/2003	Brazil ANP 07/2008
Na + K	mg/kg	122.35	111.56	24.27	5 max	5 max	5 max
Ca + Mg	mg/kg	1.8	1.69	1.81	5 max	5 max	5 max

The results show that Na + K content in Palm kernel, Neem and Palm biodiesel samples are 122.35, 111.56, 24.27 mg/kg respectively. These values exceeded the set limit of 5 mg/kg for Na + K content in ASTM D6751, EN/14214, and ANP 07 biodiesel specifications. The Ca + Mg content in the sample as outlined above are 1.8, 1.69 and 1.81 mg/kg respectively. These sums are below the limit value of 5 mg/kg for alkaline-metal content of biodiesel. It is also clear from the results in Table 3 that biodiesel from Palm kernel oil feedstock had the highest cumulative elemental contamination while Palm oil had the least cumulative elemental contamination.

3.3 Fuel Quality Parameters of the Biodiesel samples

The physicochemical/fuel quality parameters of the biodiesel samples determined are given in Table 4.The kinematic viscosity of the Palm kernel oil derived biodiesel of 5.21 mm^2/s was within the range of the fuel standard ASTM D6751- 02; 1.9 – 6.0 mm^2/s. This parameter was slightly higher for Neem and Palm derived biodiesel at 6.30 mm^2/s and 6.48 mm^2/s respectively. The specific gravity values of 0.87, 0.9 and 0.88 for Neem, Palm and Palm kernel biodiesel were all close to the specified standard of 0.88 Interestingly, the flash points.

Table 4 Comparison of fuel properties of biodiesel samples with fuel quality standards

Property	Fuel Quality Standards		Neem Biodiesel	Palm Biodiesel	P.K.O Biodiesel
	ASTM D 975 (Diesel)	ASTM D6751 (Biodiesel)			
Kinematic Viscosity mm^2/s @ 40°C	1.3 – 4.1	1.9 – 6.0	6.30	6.48	5.21
Specific Gravity	0.85	0.88	0.87	0.90	0.88
Flash Point (°C)	60 – 80	130.00 min	154	162	151
Cloud Point (°C)	-15 – 5	-3 – 12	-2	2	-3
Pour Point (°C)	-35 – (-5)	-15 – 10	-4.5	-1	-5
Acid Value mg/KOH/g	–	0.8 Max	0.05	0.28	0.04
% Moisture (w/w)	–	0.05 Max	Nil	Nil	Nil
% Yield (w/w)			64	61	77
Colour			Bright Golden Yellow	Bright Golden Yellow	Bright Golden Yellow

4. CONCLUSION

The determination of the Na + K and Ca + Mg in biodiesel is a necessary step in biodiesel characterization for quality assurance. This study has been able to determine this content for biodiesel samples produced at the Chemical Analysis Laboratory of the Projects Development Institute (PRODA) Enugu. The results showed that while the alkaline earth metal content (Ca + Mg) of the samples were within the limit values of 5 mg/kg, the alkali metal content (Na + K) of the samples were above the limit value of 5 mg/kg. This result would enable the organization adapt suitable process conditions which will allow the alkali metal content in biodiesel to be reduced to concentrations below the limit of these test methods. This would help in producing biodiesel samples that conform to specifications and which would eventually become commercial success.

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