Heavy Metal Analysis of Blends of Methyl Esters Obtained from Four Virgin Tropical Seed Oils

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Abstract: ***This paper reports the presence of heavy metals in some prepared blends of methyl esters (biodisel) obtained from four virgin tropical seed oils. The seeds were obtained from Telferia occidentals Hook F, (TVO) and Hura crepitians L (HVO) and two edible oils; Cucumeropsis manii (CSVO) and Canarium schweinfurthii Engl (CVO). Oils were extracted, degummed and methyl esters (biodisel) prepared. The Methyl esters (ME) was then blended with petrol diesel (AGO) to form different proportions as follows; B5, B10, B20 and unblended biodiesel (B100) respectively. Heavy metal analysis was done on the unblended and blended biodiesel proportions using Perkin Elmer Instrument, Analyst 400 Atomic Absorption Spectrometer. From the results of the study, iron (Fe) was absent in all the samples except TVO-ME (8.438ppm). Lead, nickel was also absent in all samples. Traces of Cadmium was found in HVO-ME (0.064ppm). Copper was present in all the B100; TVO-ME. HVO-ME, CSVO-ME, and CVO (0.418, 0.915, 0.374 and 0.924 ppm) respectively. Zinc was present in AGO and in all the B100 except in CVO-ME. Zinc was present at various concentration (ppm) except CVO-ME. Comparatively, the levels of Zn were highest in the blends Comparing the properties of the blends i.e B5, B10, B15 and B20 to B100 and AGO. Generally the blends have less of the metals than AGO. Hence it is advisable to use blends of methyl esters/Diesel (AGO).***

Keywords: Heavy Metal, Methyl Esters, Seed Oils, Virgin Tropical

1. Introduction

Heavy metals are defined as any metallic element that has relatively high density and is toxic even at low concentrations; or a group of metals and metalloids with atomic density greater than 4g/cm^3 or 5 times greater than water [1] – [7]. These metals are stable and cannot be metabolized by the body. When ingested they are converted to their stable oxidation states in the acid medium of the stomach, (Zn^{2+}, Pb^{2+}, Cd^{2+}, As^{2+}, Hg^{2+}, Ni^{2+}, Mg^{2+}, Cr^{3+}, Cr^{6+}) and they combine with the sulfhydryl groups of the bodies bio-molecules such as proteins and enzymes to form strong and stable chemical bonds [8]. Metal uptake by plant can cause negative effect on crop growth and yield. Even a reduction of crop yield by a few percent could lead to a significant long-term loss in production and income. Nickel is not known to accumulate in plants or animals. Ni is an element that occurs in the environment only at very low levels and is essential in small doses, but it can be dangerous when the maximum tolerable amounts are exceeded. This can cause various kinds of cancer on different sites within the bodies of animals, mainly of those that lives near refineries. The major sources of Nickel contamination in the soil are metal plating industries, combustion of fossil fuels, and nickel mining and electroplating. It is released into the air by power plants and trash incinerators and settles to the ground after undergoing precipitation reactions. It usually takes a longtime for nickel to be removed from air [9]. In general, plants do not absorb or accumulate lead. However, in soils testing high in lead, it is possible for some lead to be taken up. Studies have shown that lead does not readily accumulate in the fruiting parts of vegetables and fruits crop (e.g. corn, beans, squash, tomatoes, strawberries and apples). Higher concentrations are more likely to be found in leafy vegetables (e.g. carrots). Most of the risk from lead contamination comes from soil or dust deposits on the plants rather than from uptake of lead by the plant [10]. Cadmium is produced as an inevitable by-product of Zinc and occasionally leads refining. The application of agricultural inputs such as fertilizers, pesticides, and bio-solids (sewage sludge), the disposal industrial wastes or the deposition of atmospheric contaminants increases the total concentration of Cd in soils and the bioavailability of this Cd determines whether plants Cd uptake occurs to a significant degree [11]. Copper is an essential micronutrient required in the growth of both plants and animal. In plants, Cu is especially important in seed production, disease resistance and regulation of water. The connection between soil and water contamination and metal uptake by plant is determined by many chemical and physical soil factors as well as the physiological properties of the crops [12]. Increase bioavailability of heavy metals may inhibit root growth and uptake of micronutrient by trees and these effects have been shown to be synergistic [13], [14]. Several studies have shown clear impact levels of heavy metals in road side sediment soil and vegetation [15] – [19]. Canarium schweinfurthii is a large forest tree, which often grows as high as 50 m tall in the Savanna and sub-Savanna belts of Nigeria. They are often cultivated for its fruits, which are edible, purplish, ellipsoid but slightly three-angled. Hura crepitans is a large forest tree often found in the tropical rain forest and Savanna regions of Nigeria. The seeds are enclosed in hard protective coat, which usually and suddenly splash open and scatters when the seeds are well dried. The tree has broad leaves with thorns all over its trunk. Telfaria occidentalis belongs to the family Cucurbitacae spp. It is known as ‘Ugu’ among the Igede, Idoma peoples of Benue State and the Igbos of Nigeria. There is tremendous genetic diversity within the family, and range of adaptation for Cucurbits species includes tropical and subtropical regions and deserts. The genetic diversity in Cucurbitacae extends to both vegetative and reproductive characteristics. Telfaria occidentalis has become an important medicine source in the last decades. Cucumeropsis manii (white melon) is one of the species of melon commonly found in Nigeria. The seeds are edible and are usually used in preparation of soup among different tribes. The paper is aimed at quantifying the amount and kinds of heavy metals present in methyl esters and blends obtained from the aforementioned four tropical seed oils as these metals affect crop yield, methyl ester degradation during storage, material compatibility and solvency properties of methyl esters and their blends.

2. Materials and Methods

2.1. Test Materials/Sample Collection

Canarium schweinfurthii seeds were obtained from Jos, Plateau State during the dry season. The seeds were sun dried for about two weeks to remove moisture after which they were ground into coarse powder and ready for extraction. While Hura crepitans, Telfaria occidentalis and Cucumeropsis manii seeds were collected from Makurdi metropolis, Benue State between December and January. All the seeds were extracted from the bulb and dried to a constant weight after which the mesocarps were removed by dehulling. The dried seeds were pounded into coarse powder and ready for extraction. The seeds were identified by a botanist in the department of Biological Science of Benue State University, Makurdi.

2.2. Degumming of Crude Oils

The oils were degummed to remove phospholipids, calcium and magnesium salts of phosphatidic and lysophasidic acids which are strong emulsifiers that inhibit the separation of the glycerol which lowers the yields of neutral oil. In degumming, the crude oil was mixed with about 3% of warm water and the mixture was agitated mechanically for 30 min at 70^oC. This hydrates the phospholipids and gums thus making them insoluble in the oil. They were thereafter separated by settling.

2.3. Production of Biodiesel Fuels

The 100 mL of pretreated oil was measured and poured into a large beaker and heated to a temperature of 110^oC using bunsen burner to remove the remains of solvent or moisture content. The heated oil was cooled to $38/55^oC$ and poured into a blender fabricated for use as a reactor, With the reactor still switch off, methoxide was prepared by weighing 1g of KOH or NaOH in a pet bottle and a calculated volume of methanol was added based on the desired alcohol/oil molar ratio (4:1, 6:1 and 9:1) and shaken to dissolve the catalyst completely. The prepared methoxide was emptied into the oil and properly covered to prevent air from entering into the mixture. The mixture was reacted for the required time of mixing (5 or 30mins) after which the blender was switched off and the mixture immediately transferred into a separating funnel and closed tightly. The mixture was allowed to settle for 24 h after which a dark color glycerin settled at the bottom while a pale liquid layer which is the methyl ester separated at the top [20].

2.4. Biodiesel Separation

Upon completion of reaction, two major products were formed, glycerin and biodiesel. The clear liquid, methyl ester (biodiesel) found at the top layer was decanted into a graduated beaker (NBB).

2.5. Biodiesel Washing

The biodiesel was turned into a separating funnel after which an equal amount of distilled water was added. The separating funnel was gently swirled severally and allowed to stand for some minutes and the water drained off from the bottom of the funnel by turning on the tap of the separating funnel. The tap was turned off when it reached the methyl ester. This procedure was repeated twice to ensure complete washing. After washing, the biodiesel was dried by heating [21].

2.6. Blend preparation (derived biodiesel with petrol diesel)

Blending of biodiesel was done using an in – tank method of petroleum blending, the biodiesel obtained after thermo-physical screening was blended with AGO obtained from fuel station at different proportions. They include, B5, B10, B20 and unblended biodiesel (B100). The blends were centrifuged for homogeneity before proceeding with fuel analysis using ASTM standards.

Figure 1: samples of blends of petro-diesel/ biodiesel

2.7 Determination of trace metals (Perkin Elmer Instrument, Analyst 400 Atomic Absorption Spectrometer)

The equipment air compressor was drained, the hallow cathode lamb for test was installed and power was turn on to air compressor (the pressure output to the line was 68 psi). The spectrometer was then switch on. After initialization the lamb icon was clicked for the lamb of interest. When the setup was completed the energy value came up and the lamb window was closed. The elements of choice were selected. The acetylene cylinder was opened and the final output was ensured to be 14 psi, the flame was then ignited. To run the samples, oils were ashed, digested, and filtered. Standards were prepared, aspirated and analysed before analysing the samples.

3. Results Discussion

Table 1: Levels of Heavy Metals (ppm) in the sample

Sample	*Fe*	*Pb*	*Zn*	*Ni*	*Cd*	*Cu*
HVO-ME	Nil	Nil	3.309	Nil	0.064	0.418
TVO-ME	8.438	Nil	0.565	Nil	Nil	0.915
CVO-ME	Nil	Nil	Nil	Nil	Nil	0.374
CSVO-ME	Nil	Nil	1.539	Nil	Nil	0.924
HVO-ME B5	Nil	Nil	11.175	Nil	Nil	Nil
HVO-B10	Nil	Nil	10.404	Nil	Nil	Nil
HVO-B15	Nil	Nil	3.545	Nil	Nil	Nil
HVO-B20	Nil	Nil	3.183	Nil	Nil	Nil
TVO-ME B5	Nil	Nil	8.510	Nil	Nil	Nil
TVO-B10	Nil	Nil	8.374	Nil	Nil	Nil
TVO-B15	Nil	Nil	6.256	Nil	Nil	Nil
TVO-B20	Nil	Nil	4.799	Nil	Nil	0.466
CVO-ME B5	Nil	Nil	8.573	Nil	Nil	Nil
CVO-B10	Nil	Nil	4.244	Nil	Nil	Nil
CVO-B15	Nil	Nil	3.148	Nil	Nil	Nil
CVO-B20	Nil	Nil	1.673	Nil	Nil	Nil
CSVO-ME B5	Nil	Nil	11.526	Nil	Nil	Nil
CSVO-B10	Nil	Nil	10.603	Nil	Nil	Nil
CSVO-B15	Nil	Nil	8.974	Nil	Nil	Nil
CSVO-B20	Nil	Nil	6.669	Nil	Nil	0.690
AGO	Nil	Nil	12.078	Nil	Nil	Nil

The result of heavy metal analysis of blends of methyl esters obtained from four virgin tropical seed oils are presented as follows in Figure 2 and Table 1.

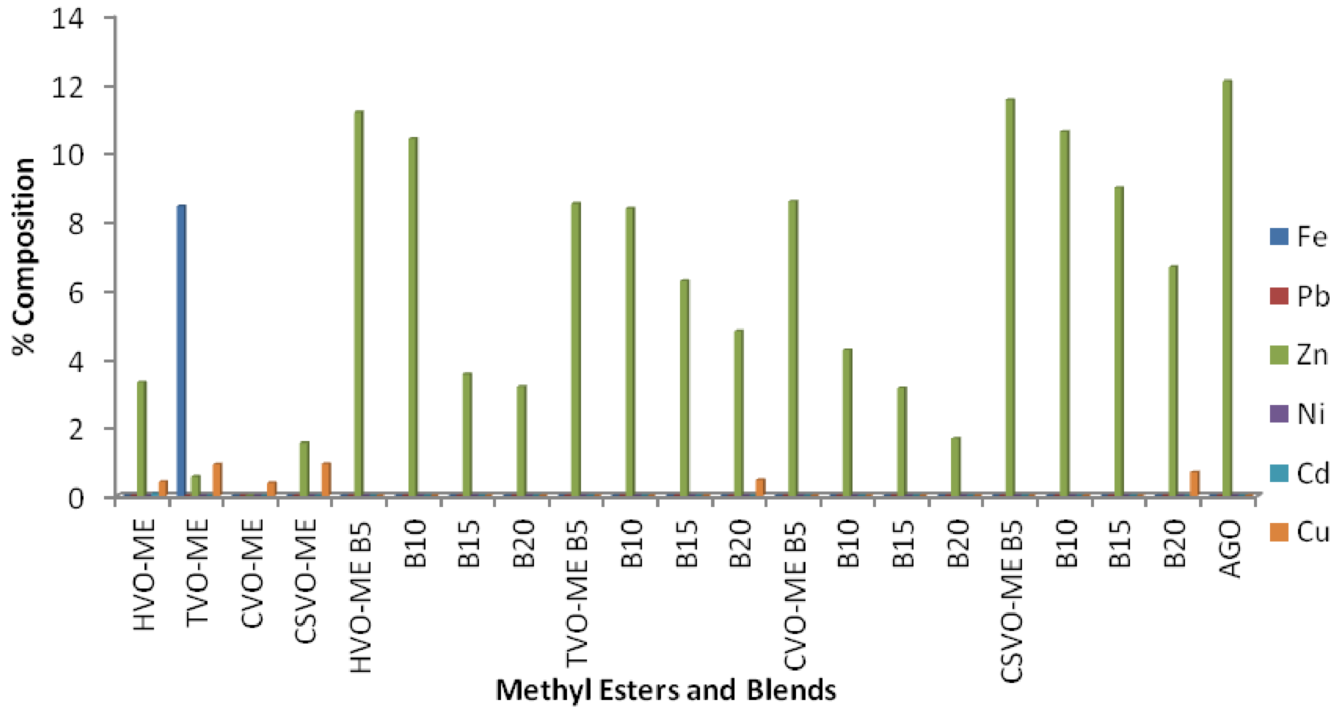

Figure 2: Heavy metal contamination of Methyl Esters and Blends

3.1. Discussion

This analysis was carried out because certain metals such as copper, brass, bronze, lead, tin and zinc accelerates the degradation process and form even higher levels of sediments than would be formed otherwise [22] and most plants can absorb such metals which may trap in the seeds.

The amounts of these metals were determined using the AAS and Fig. 2 shows their various amount in the blend prepared. Iron (Fe) was absent in all the samples except TVO-ME (8.438ppm). This is because research has shown Fe to be present in Telfaria occidentalis hence the vegetable is used as a blood volume extender in Nigeria. Lead, nickel was also absent. Lead in general is not absorbed or accumulated in plant except when in high amount in soils. Lead does not accumulate in fruity parts of crops. Most of the risk from Lead on plants is rather from deposits on plants [10]. In this case these plants are shown to contain no lead deposits. Nickel on the other hand maybe absent because the samples were not obtained from areas that are near sources of Nickel except power plant which were minimal. Traces of Cadnium was found in HVO-ME (0.064ppm). The bioavailability of Cadnium determines whether plant uptake occurs in a significant degree [11]. Copper was present in all the B100; TVO-ME. HVO-ME, CSVO-ME, and CVO- ME (0.418, 0.915, 0.374 and 0.924) in ppm respectively. This is because copper is important naturally in seed production, hence present in all the seeds oils [12]. Only very small amount of methyl esters were used in the blends hence the absence of copper in most of the blends. Traces were also found in B20 (TVO-ME) and B20 (CSVO-ME)because of the amounts present in their corresponding B100 (TVO-ME and CSVO-ME). Zinc was present in AGO and in all the B100 except in CVO-ME, as showed in Fig. 2 and Table 2. Zinc was notably absent in CVO-ME. The amount was higher ranging from B5 to B20 as B5 possesses properties closer to AGO which had the highest Zinc content.

Storage stability refers to the ability of the fuel to resist chemical changes during long time storage. These changes usually consist of oxidation due to contact with oxygen from the air. The changes can be catalyzed by the presence of these metals (including those making up storage container) and light. Sediment may consist of suspended rust and dirt particles or it may originate from the fuel as insoluble compounds formed during fuel oxidation. These sediments may plug fuel filters and contribute to the formation of deposits on fuel injectors and other engine damage; sediments level may increase over time as the fuel degrades during extended storage [23]. Material compatibility is also an important properties to consider with biodiesel (methyl enters). Oxidation and sediment production in either biodiesel or diesel can be initiated by contact with brass, bronze, copper, stainless steel or aluminum equipment in the processing, while aluminum, steel, Teflon and fluorinated polyethylene and polypropylene can be used for construction of storage tanks [22]. While biodiesel is only a mild solvent, it does have higher solvency properties than diesel fuel. Due to this property, residual sediments in diesel storage tanks or vehicle fuel tank can be solvated by biodiesel (B_{100}). The solvent properties of biodiesel are mitigated by the use of biodiesel in blends with diesel fuel. Typically, 20% or less blends of biodiesel in diesel will nearly completely dilute the solvency effect. However, this solvency effects should be considered if pure biodiesel is stored in a tank that was previously used for standard diesel [23]. Hence it is advised to use blends of methyl esters/Diesel (AGO) as the results indicates less amount of heavy metals in the lends as compares to AGO.

4. Conclusion

The presence and amount of heavy metals present in the B_{l00} and blends obtained from these form tropical seed oils have been established. These plants should therefore not be grown in areas that are prone to the presence of these heavy metals such as Zn, Cu, and Cadmium to avoid negative effect on crop growth and yield. The B_{l00} and blends obtained can be stored over a longer period of time with minimum degradation due to the minimal of heavy metals presence in them. The B_{l00} and blends will not be compatible with material constructed with Zn, Cu and their alloys as these will accelerate or catalyze oxidation process. Solvency properties of B_{100} can be greatly enhanced in the blends as the result of the analysis shows reduced amounts of heavy metals in the blends compared to AGO.

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