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Note

Evaluation of chosen fruit seeds oils as potential biofuel

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A b s t r a c t. Oils available in mango, tangerine and African star seeds were extracted and characterized to determine their fuel worthiness for biofuel production. Furthermore, the fuel properties of the three oils were within the range observed for some common oil seeds like rapeseed, soybean and sunflower, which are widely sourced for the production of biodiesel on an industrial scale. The low iodine values of the oil extend their applications as non-drying oil for lubrication purposes, however, the fuel properties exhibited by the oils enlist them as potential oil seeds for the production of biofuel and further research on the improvement of their properties will make them suitable biofuel of high economic values.

K e y w o r d s: fruits seed oil, biofuel, fuel properties

INTRODUCTION

The concern for fast depletion of petroleum oil and its environmental impact has shifted interest to alternative sources of fuels, particularly biofuels, which are renewable and environmental friendly (Demirbas, 2008). Thus, varieties of virgin, non-edible and waste vegetable oils have been sourced for the production of biofuels (Maniak *et al*., 2009). The choice of biofuel over diesel fuel includes its portability, availability, renewability, higher combustion efficiency, higher cetane number, higher biodegradability, high flash point, inherent lubricity, lower sulfur and aromatic contents (Knothe *et al.*, 2005).

Some of the widely sourced oil seeds for biofuels include rapeseed, soybean, palm, sunflower, jatropha, and castor seeds (Meher *et al.*, 2006). However, some of the oils studied were characterized by higher viscosity, lower volatility, lower energy content, higher nitrogen oxide (NOx) emission rates, lower engine speed, reactivity of unsaturated hydrocarbon chains, higher cloud point and pour point (Enweremadu and Alamu, 2010). All these are contrary to the qualities found in the convectional diesel fuel, in the light of this, virgin oilseeds are studied for their potentials as viable source for biofuel production.

African star apple (*Chrysophyllum albidum*) is a large berry fruit of plant family called *Sapotaceae* widely found in some West and Central African countries (Bada, 1997). The commercial value of the fruit is attracting interest particularly application of its seed oil as well as roots and leaves for medicinal purposes (Bada, 1997). Mango (*Mangifera indica*) fruit, on the other hand, is a drupe with a single seed, surrounded by yellowish or orange fibrous flesh, rich in vitamins. This tropical fruit tree thrives well in Asia and Africa continents and its shapes, sizes and colour depend on the variety (Nzikou, 2009). Tangerine fruit belongs to the family of *Citrus genus* and the sweet (*Citrus sine sis*) is the most widely grown of the citrus trees and the fruit is either eaten fresh or made into juice. The selected seeds contributed immensely to solid agricultural wastes found in most the towns where they are grown and consumed. This study examined the properties of oils obtained from African star apple, mango and tangerine seeds for their potential application in the production of biofuel.

MATERIALS AD METHODS

The African star apple, mango and tangerine seeds were sourced within the vicinity of Ogbomosho Township, Oyo State, Nigeria, shortly after the seasonal period, which fall between May and July 2009. The reagents used were of analytical grade (BDH analar) supplied to the Laboratories of Ladoke Akintola University of Technology, Ogbomosho.

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The African star apple seeds were de-coated, the endocarps were sun-dried for 72 h, milled and screened to partly fine, and 100 g was soxhlet-extracted with ethanol for 6 h. Dark brown oil was obtained and the excess solvent was distilled off using a rotary evaporator (RE-52A, Shanghai Ya Rong Biochemistry Instrument Factory, Shanghai) at 45°C, weighed and the percentage yield was determined. The process of extraction of the oil from mango seeds involved de-hulling, sun-drying of the endo-carps to constant mass for 120 h and further processed as applicable to the African star apple above. The tangerine seeds were sun-dried, milled and screened as stated above, and 30 g of the milled seeds was subjected to soxhlet extraction described above using n-hexane. The analysis and characterization of the oils extracted from the selected seeds include pH, refractive index, retention factor, congealing temperature, flash point, heat of combustion, flame nature, solvent miscibility, acid value, free fatty acid, saponification value, iodine value, peroxide value, peroxide value, peroxide value, and specific gravity were done by standard methods (Ainie *et al.*, 2005).

RESULTS AND DISCUSSION

The results of the analysis and characterization of the oils derived from African star apple, mango and tangerine seeds were shown in The colours of oils extracted from the Africa star apple, mango and tangerine seeds were dark brown, golden yellow and light brown while their percentage yield were 16.8, 38.9, and 33.4, respectively (Table 1). The oil yields from the mango and tangerine seeds were higher than the yield (18%) obtained for soybean seed but the yields of the three oils were above the yields of similar seeds like *D. edulis* (15.3%), *N. imperialis* (8.0%) and *L.Owarieusis* (6.4%) in the region (Akubugwo and Ugbogu, 2007). The oil yield (16.8%) obtained for African star apple seed in this study was higher than the yield (12%) reported by (Akubugwo and Ugbogu, 2007).

The refractive index of African star apple, mango and tangerine seed oils, obtained at 25°C, were 1.61, 1.45, and 1.53, respectively. The refractive index of African star apple and tangerine seed oils, were above the refractive index (1.475-1.485) obtained for most oils and this indicates that these oils are thicker than most non-drying oils. The tangerine seed oil had the highest specific gravity (0.936) at 20°C while the specific gravities of African star apple and mango seeds oils were 0.877 and 0.885 respectively, and this show they are all less dense than water (Akinhanmi *et al.*, 2008).

The specific gravity of oils generally characterizes the fluidity of oils in automobile engines and the values obtained in this study are within the ranges acceptable for biodiesel (Enweremadu and Alamu, 2010). The pH of the African star apple (5.27) mango (5.44) and tangerine seeds oil (3.56) were generally low which indicate presence of a reasonable amount of free fatty acids in the oils and this is a potential characteristic of their utilization as fuel oil. The retention factor (RF) of the oils were 4.86, 3.78 and 1.65 cm for African star apple, mango and tangerine seeds, respectively and showed appreciable degree of purity of the oils. The iodine value (IV) indicates the level of unsaturation in oils samples (Fakou *et al.*, 2009) and the values obtained for African star apple, and mango seed oils were 67.60 and 76.40 mg Na_2SO_3 g^{-1}, respectively, which were below 100 mg Na_2SO_3 g^{-1} and thus classified them as non-drying oils suitable for lubricant industry (Oladimeji *et al.*, 2001). Moreover, these values were lesser than the lowest IVs of oils obtained from peanut kernel, cottonseed and rapeseed (Table 2). However, the IV of Tangerine seed oil (109.6 mg Na_2SO_3 g^{-1}) placed the oil in between the drying and semi-drying oils (Oladimeji *et al.*, 2001) and fell within the ranges observed for cottonseed, peanut kernel, rapeseed and sesame seed oils (Table 2). Furthermore, Enweremadu and Alamu (2010), reported that such low IV indicates low degree of unsaturation of the oils as non-drying oils, since they are below a range of 220-270 mg Na_2SO_3 g^{-1}. Moreover, Fakou *et al.* (2009), noted that very high iodine value often reduces the stability of the oil because of oxidation.

T a b l e 1. Characteristics of African star apple seed, mango seed and tangerine seed oils

Oil characteristics	Seed oil		
	African star apple	Mango	Tangerine
pH	5.27	5.44	3.56
Refractive index at 25°C	1.61	1.45	1.53
Retention factor (cm)	4.86	3.78	1.65
Congealing temperature (0°C)	-12 to -28	-18 to -30	-7 to -18
Flame nature	Non-sooty	Slightly sooty	Non-sooty
Product % yield	16.8	38.5	33.4
Specific gravity at 20°C	0.878	0.885	0.936

T a b l e 2. Selected oil properties of plant oils used for production of biofuel

Oil	IV (mg N_2SO_3 g^{-1})	HC (KJ kg^{-1})	FP (°C)	AV (mg KOH g^{-1})	PV (mg N_2SO_3 g^{-1})	SV (mg KOH g^{-1})
Cottonseed	90-119a	3 9468a	234a	0.07b	64.8b	207.71c
Linseed	168-204a	3 9307a	241a	NA	NA	188.71c
Peanut kernel	80-106a	3 9782a	271a	0.20b	82.7b	199.80c
Rapeseed	94-120a	3 9709a	246a	1.14b	30.2b	197.07c
Safflower	126-152a	3 9519a	260a	NA	NA	190.23c
Sesame	104-120a	3 9349a	260a	NA	NA	210.34c
Soybean	117-149a	3 9623a	254a	0.20b	44.5b	220.78c
Sunflower	110-143a	3 9575a	274a	0.15b	10.7b	191.70c
African star apple seed	67.6±0.3d	52 230±7.6d	178±1.0d	0.26±0.01d	36.96±0.03d	327±0.5d
Mango seed	76.4±0.1d	34 583±11.7d	173±0.0d	0.32±0.01d	10.08±0.02d	143±1.0d
Tangerine seed	109.6±0.4d	34 800±0.0d	164±1.0d	0.07±0.002d	86.80±0.15d	153.6±0.08d

FP – flash, point; HC – heat of combustion; AV – acid value; SV – saponification value; IV– iodine value; PV – peroxide value; NA – not available. a – Knothe *et al*. (2005), b – Fangrui and Hanna (1999), c – Demirbas (2008), d – results of this study.

The acid value (AV) of oil indicates the content of free acid in the oil samples and it is as an important property that influences the shelf life of the oil (Predojevic, 2008). The AV of African star apple, and mango seed oils were 0.26 and 0.32 mg KOH g^{-1}, respectively and were higher than the AVs of cottonseed (0.07 mg KOH g^{-1}), peanut kernel (0.20 mg KOH g^{-1}), rapeseed (1.14 mg KOH g^{-1}), soybean (0.20 mg KOH g^{-1}), and sunflower (0.15 mg KOH g^{-1}) (Table 2). The AV of tangerine seed oil was 0.70 mg KOH g^{-1}, which is the same obtained for cottonseed oil, however the AV of the oils obtained in this study were lower than the AV (1.14 mg KOH g^{-1}) observed for rapeseed oil. High AV favours the choice of oil seeds for the production of biodiesel because most oils with low AV are mainly edible oils fit for human consumption and food processing industries (Predojevic, 2008). Generally, the maximum AV recommended for biodiesel is 0.5 mg KOH g^{-1} (JUS EN 14214, 2004) and the AV of biodiesel to be produced from these oils is expected to be close to the values of their raw oils.

Peroxide Value (PV) measures the rancidity of an oil sample and 10 mg Na_2SO_3 g^{-1} has been accepted as convectional for majority of the oils (Nwobi *et al*., 2006). The PVs of African star apple (36.96 mg Na_2SO_3 g^{-1}) and Tangerine (86.8 mg Na_2SO_3 g^{-1}) compared well with those obtained for cottonseed (64.8 mg Na_2SO_3 g^{-1}), peanut kernel (82.7 mg Na_2SO_3 g^{-1}), rapeseed (30.2 mg Na_2SO_3 g^{-1}), and soybean (44.5 mg Na_2SO_3 g^{-1}) (Table 2) and all showed high rancidity value. The PV of mango seed oils was 10.08 mg Na_2SO_3 g^{-1} and compared very well with PV of sunflower oil which has been sourced as oil seed for the production of biodiesel (Freedman *et al*., 1984) and as such cannot easily become rancid with this value, which is less than 40.

Flash point (FP) of oil is the minimum temperature at which the oil becomes flammable and high value of FP suggests that the oil is less susceptible to fire related hazard in transportation, storage and utilization. The FP of the African star apple (178°C) mango (173°C) and tangerine seeds oil (164°C) were generally lower than other seed oils shown in Table 2, which indicate that they are safer to handle. The acceptable FP of biodiesel ranges between 130-131°C (Chogkhong *et al*., 2007), and it is, however, expected that after the transesterification process the FPs of the oils in this study will compare well with most seed oils listed in Table 2.

Heat of combustion of oil sample indicates the energy contents of the oil when subjected to burning and related to its maximum power output (Song, 2000). The heat of combustion of the mango and tangerine seed oils in this study were, approximately, 34 583 and 34 800 KJ kg^{-1}, respectively, and were lesser than the values obtained for similar seed oils as well as the range (37 270-40 480 KJ kg^{-1}) stipulated for most oils (Demirbas, 1998) (Table 2). This suggests that the two oils can be used in engines designed for lesser tasks particularly those involving less torque. The heat value (52 230 KJ kg^{-1}) of African star apple seed oil was equally well above this range and the heat value 300 KJ kg^{-1} of D2 fuel (Demirbas, 1998) though this oil may result in overheating of the engine, however, it may be reduced after subjecting the oil to transesterification process.

The saponification value (SV) of the African star apple, mango and tangerine seed oil were 327, 143 and 153.6 mg KOH g^{-1}, respectively which is similar to trend observed in the heat of combustion above. However, the saponification values of the oils are expected to show a reverse relationship to their heat of combustion, as observed by Demirbas (1998), but the results obtained in this study is on the contrary. Oils with high saponification values, like African star apple seed oil, are generally suitable for soap production.

CONCLUSIONS

1. The percentage oil yields obtained from the African star apple, mango and tangerine seeds were comparable to biofuel-sourced oil seeds and this shows the application for the biofuel production in commercial scale.

2. The low iodine value (IV) obtained for African star apple, and mango seed oils further indicate their potential as non-drying oils suitable for lubricant industry.

3. Similarly, low acid value (AV) of oils obtained indicates their resourcefulness as feedstock for the production of biodiesel.

4. The lower flash point (FP) of the African star apple, mango and tangerine seeds oil, shows that they are safe to handle and for storage.

5. The relatively lower heat of combustion of the mango and tangerine seed oils suggests that the two oils can be applied in engines involving less torque.

6. The saponification values of oils are inversely related their heat of combustion, but the results obtained in this study are on the contrary.

7. Further study will include the determination of oil properties such as cetane number, fractional composition, viscosity, vapor pressure, lubricity, corrosive, self-ignition temperature, the cold filter plugging point, in order to assess possibility of using these vegetable oils or their esters to power internal combustion engines.

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