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POTENTIAL OF SEED OIL OF HILDEGARDIA BARTERI (MAST.) KOSTERM FOR BIODIESEL PRODUCTION

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ABSTRACT

This study analysed seed oil of *H. barteri* as a source of biofuel. Mature fruits of *H. barteri* were collected from two mother trees and dehulled, oven and sun-dried and milled. Mechanical extractor and solvent extraction (N-Hexane) was used to obtain oil and analysed for presence of C, H, O, S, N, Pb, Cd, Ni, and Co; physicochemical properties, calorific value. Oil yields ranged from 23.15-30.53% for mechanical and solvent methods. Specific gravity, cloud point, conradson carbon, acid value and iodine values ranged from 0.83-0.85, 7.4-8.3^{0}C, 0.16-0.27%, 31.85-33.95 mgKOH and 57.3-61.8 respectively while C, O, H, N and S contents were generally higher in oil obtained by mechanical extraction. The Pb level was least (0.007%) in solvent extracted oil and highest (0.023%) in sun-dried mechanically extracted oil. Iodine values of solvent and mechanically extracted samples were 61.85 and 58.6 respectively. Calorific value of sun-dried solvent extracted oil was slightly higher (36,140kj/kg) than the oven-dried (35,690kj/kg). Results obtained showed promising indication that the seed oil of *Hildegardia barteri* could be used for production of biodiesel.

I. INTRODUCTION

The use of energy either domestically or industrially has been one of the common things all over the world. The different forms of energy which are categorized as either renewable or non-renewable, all channels down to the production of either primary goods (i.e. processing of raw foods into consumable forms) or/and secondary goods (like production of simple tools, machines) for the survival of man [1].

As energy plays a fundamental role in shaping human condition, it has also been argued that it is the key "to the advance of civilization," and that the evolution of human societies is dependent on the conversion of energy for human use [2]. Based on this fact, the quest for energy for human use is continuous and researches tends towards the production of renewable energy that would bring about improved air quality, lower consumption of fossil fuel and reduce green-house gas emission as reported by CFS (2012) [3]. This therefore informs the identification and production of energy from suitable biomass sources (such a`s animal fat, algae, plant seed oil and crops) that can provide high energy outputs- an alternative to the conventional fossil fuel sources.

II. LITERATURE REVIEW

II.1 BRIEF DESCRIPTION OF PLANT SPECIES

Hildegardia barteri (Mast.) Kosterm tree plant belongs to the family Malvaceae. It is primarily an ornamental tree in West Africa, grown only for its bright beautiful flowers which mature into one-seeded pods during the dry season [4]. Though edible, only few parts of West Africa are observed to consume the kernels either raw or roasted like peanuts [5], or used as condiments in traditional food preparations because of its oil content [6]. This research is however chosen and carried out to maximize the inherent potentials that could be derived from fruits or seeds of lesser used species such as *Hildegardia barteri* in order to avoid wastage of biomass resources. The energy value and other essential parameters that ensure a consistent quality of fuel were determined from the oil extracted from the fruits of *H. barteri.*

III. MATERIALS AND METHODS

Sample preparation: Fruits of Hildegardia barteri were collected from the premises of Department of Agronomy, University of Ibadan, de-hulled, dried using two methods-sun-drying (SD) and oven drying (OD), weighed, milled and packaged in ziplock bags, prepared for the extraction of oil content using soxhlet extraction (SE) with N –hexane solvent and mechanical method (ME). Samples collected were (OD+SE, SD+SE, OD+ME and SD+ME) results of interactions between the two methods of drying and two methods of extractions.

Experimental Design: For objectives of this study, a 2x2 factorial experiments in a completely randomized design was used for the statistical analysis in order to evaluate the significant difference of parameters analyzed among oil samples. Factor A which was at 2 levels represents the drying methods while factor B represents the methods of extraction which is also at 2 levels.

Determination of percentage (%) yield: The percentage yield was calculated using the equation shown below [7]:

$$\%\ Oil\ yield = \frac{Weight\ of\ oil}{Weight\ of\ unextracted\ milled\ seed} \times 100 \quad (1)$$

Elemental Analysis of Seed Oil

Determination of Carbon, Hydrogen, Oxygen and Nitrogen.

The following procedure was used to determine the essential elements except for sulphur.

2g of oil sample was weighed into platinum crucible and placed in a Leibig-pregle chamber containing Magnesium percolate and sodium hydroxide. The sample was burnt off to produce carbondioxide and water. The CO2 was absorbed by Sodium hydroxidewhile the water was absorbed by magnesium percolate. The amount of water and CO2 were calculated by difference.

$$\%\ C \quad \frac{a \times 0.2727}{Weight\ of\ unextracted\ milled\ seed} \times 100 \quad (2)$$

$$\%\ H = \frac{b \times 0.117}{Weight\ of\ unextracted\ milled\ seed} \times 10 \quad (3)$$

$$\%\ O = 100 - (\%C + \%H) \quad (4)$$

Determination of nitrogen

Nitrogen content was determined using kjeldahl method; the formula used for calculating % N was:

$$\%\ \mathrm{N} = \frac{((\mathrm{S} - \mathrm{B}) \times \mathrm{N} \times 0.014 \times \mathrm{D})}{(\text{Weight of milled seed} \times \mathrm{V}) \times 100} \quad (5)$$

Where,
S = Sample titration reading
B = Blank titration reading
N = Normality of HCl
D = Dilution of sample after digestion
V = Volume taken for distillation
0.014 = Milli equivalent weight of Nitrogen

Procedure for determining Sulphur from the digest

5ml of the digest was pipette into a 100ml beaker and 10ml of distilled water was added and mixed thoroughly to a complete homogenized solution. Then 1ml of 1% Barium gelatin solution was added to precipitate the sulphur. Working standard of sulphur was prepared from range 0-50mg/l and treated similarly like sample.

Absorbance of standard as well as sample was read on a spectronic 21D spectrophotometer at a wavelength of 420nm.

Sulphur in mg/100g was calculated using the formula:

$$Sulphur = \text{Absorbance} \times \text{gradient factor} \times \text{dilution factor} \quad (6)$$

Heavy metals Analysis

Heavy metal analysis of the oil was determined according to the methods of ASTM 3174-76 [8] with the use of the atomic absorption spectrophotometer (AAS) to determine elements such as Pb, Cd, Ni and Co. 0.5g of each sample was weighed into a beaker and 10ml of an acid solution (Nitric/perchloric acid) in ratio 1:2 was added to the sample in the beaker. Then it was allowed to undergo heating on a hot plate at 105°C for an hour. The colour change while heating was observed to be from brown to clear colourless. The digest at this point was allowed to cool. The digest was then read on the atomic absorption spectrophotometer to determine the following metals.

Determination of Physicochemical properties

The extracted oil was analyzed for biodiesel physical properties after the procedures of AOCS, (1978) [9] and AOAC, (1984) [10] while the chemical properties were investigated following standard methods such as ASTM (1998) [11] and [10].

Determination of cloud point

A glass bottle containing 50ml of the oil with an inserted thermometer was immersed together in a water bath and used to measure the temperature at which crystallization begins in liquid oil. The temperature at which the thermometer was no longer visible was taken as the cloud point (ASTM D 2500).

Determination of Fire point

A 250ml conical flask containing 50ml of the oil with an inserted thermometer was placed on a heating mantle. Continuous heating was done until the oil was decomposed to point of evolution of the volatiles which proceeds so rapidly that continuous combustion occurred i.e a fire. The temperature at which this occurred was taken as the fire point.

Determination of Flash point

2g of the oil was weighed into a cylindrical metal container attached with a 0-100°C mercury in glass thermometer. The set - up was heated at a controlled rate on a Gerhadt Heating Mantle set at 105°C with a naked flame from a match stick being passed over the surface of the heated oil at regular interval of 5mins. The temperature measured by the thermometer at a point at which a flash appears at any point of the surface is known as flash point.

Determination of Specific gravity

10ml of the oil was weighed into a previously weighed empty Specific Gravity Bottle with weight W1. Weight of oil plus bottle was noted as W2. 10ml equal volume of distilled water was weighed into the same bottle and weight of bottle plus water was also noted as W3. Specific Gravity of the oil is determined by using the formula:

$$SG = \frac{(W\_2 - W\_1)}{(W\_3 - W\_1)} \quad (7)$$

Determination of Viscosity

This was measured using a viscometer and with aid of an attached water bath. Viscosities of the oils with respect to that of water at various temperatures (30, 40, 50, 60, 70 and 80°C) were determined using the equation below:

$$ɳo = \frac{(ɳw\ ρo\hat{}t)}{(ρw\ tw)} \quad (8)$$

Where,
ɳo and ɳw = Coefficients of viscosity of oil and water respectively.
ρo and ρw = Densities of oil and water, respectively
to and tw = Times of flow of oil and water, respectively

Acid value/Free Fatty Acid (FFA)

A mixed neutral solvent containing a mixture of 25ml diethylether with 25ml alcohol and 1ml of phenolphthalein solution (1%) was prepared. The mixed solution was then neutralized with 0.1M NaOH. 1g of the oil will be dissolved in a 250ml conical flask containing 25ml of the mixed neutral solvent. The mixture was heated to boiling point and shakened vigorously. The solution was cooled and then titrated with 0.1M alcoholic caustic potash solution with constant shaking using phenolphthalein as indicator until the pink colour persisted for 15sec [12] and [10]. The acid value was calculated as:

$$\text{Acid value (mgKOH/g)} = \frac{(\text{Titre value of alkali} \times 0.1\text{M alkali} \times 56.1)}{((\text{Wt of sample used})\ (g))} \quad (9)$$

%FFA was calculated by multiplying the acid value with the factor 0.503 i.e %FFA = 0.503 x acid value [13].

Determination of Calorific Value

Gross calorific value of oil was determined using a CAL 2K-ECO bomb calorimeter.

IV. RESULTS AND DISCUSSIONS

Percentage Oil Yield: Result obtained shows the mean value of triplicate analysis of the samples (Table 1).

Table 1: Percentage Oil Yield.

Source of Variation	DF	MEAN	P-Value
OD+SE	2	23.15±1.51[a]	0.0238
SD+SE	2	30.53±3.02[b]	
OD+ME	2	21.96±1.35[a]	
SD+ME	2	19.52±2.10[a]	

Source: Authors, (2020).

*Means ±SE of triplicate values with same alphabets are not significantly different; significant at p-value < 0.05.

The range of percentage oil yield obtained considerably agrees with the findings of Matchet (1963) [14]) on the suitability of oil-bearing seed that yield up to 30% for commercial oil applications.

Elemental Analysis: Result obtained from the analysis of these essential elements C, H, O, N and S, shows that all elements except for carbon and hydrogen content are lower in the oils samples (Table 2). Nitrogen and Carbon contents in mechanically extracted samples were observed to be significantly different from the solvent extracted samples. Hydrogen content in the oil samples ranged between 8.3-9.57±0.01%. No significant difference was observed in the oxygen content between the mechanically extracted and solvent extracted samples. The sulphur content which is of environmental concern, obtained in this study compares favorably with the ASTM standard [15] (0.05 % max) except for the SD+SE sample.

Table 2: Elemental analysis of seed oil.

PARAMETER	SAMPLES	MEAN	P-VALUES
% NITROGEN	OD+ME	0.16±0.03[a]	0.0001
	OD+SE	0.26±0.02[b]	
	SD+ME	0.19±0.01[a]	
	SD+SE	0.27±0.01[b]	
% HYDROGEN	OD+ME	8.49±0.01[b]	0.0001
	OD+SE	9.57±0.01[d]	
	SD+ME	8.3±0.01[a]	
	SD+SE	9.38±0.01[c]	
% OXYGEN	OD+ME	17.99±0.51[ab]	0.0001
	OD+SE	18.57±0.01[b]	
	SD+ME	17.7±0.01[a]	
	SD+SE	18.42±0.01[b]	
% SULPHUR	OD+ME	0.02±0.01[a]	0.0227
	OD+SE	0.035±0.01[a]	
	SD+ME	0.035±0.02[a]	
	SD+SE	0.065±0.02[a]	
% CARBON	OD+ME	71.29±0.01[a]	0.0001
	OD+SE	72.05±0.01[b]	
	SD+ME	71.33±0.02[a]	
	SD+SE	72.12±0.01[b]	

Source: Authors, (2020).

Means ±SE of duplicate values with same alphabets are not significantly different; significant at p-value < 0.05.

Heavy metals Analysis: Result obtained from this analysis (Table 3) shows that concentration of these heavy metals fall within the permitted range. Proportions of these heavy metals are in line with the maximum concentration permitted by USEPA, standard [16]. The lower values of heavy metals obtained in the oil sample, give basis for the exploitation of oil from *H. barteri* seed as a potential source for clean renewable biodiesel.

Table 3: Heavy metal Analysis.

		MEAN	P-VALUES		
PARAMETER	**SAMPLES**			**PARAMETER**	**FACTOR B**
Pb	OD+ME	0.017±0.002b,c	0.0003	Pb	OD+ME
	OD+SE	0.01±0.002 a,d			OD+SE
	SD+ME	0.023±0.002e			SD+ME
	SD+SE	0.007±0.001a			SD+SE
Cd	OD+ME	0.0035±0.001b	0.0174	Cd	OD+ME
	OD+SE	0.007±0.001c			OD+SE
	SD+ME	0.003±0.001b			SD+ME
	SD+SE	0.0045±0.001b			SD+SE
Ni	OD+ME	0.025±0.001a,b	0.0004	Ni	OD+ME
	OD+SE	0.029±0.001a			OD+SE
	SD+ME	0.022±0.001b			SD+ME
	SD+SE	0.034±0.002c			SD+SE
Co	OD+ME	0.012±0.001a,b		Co	OD+ME
	OD+SE	0.014±0.001b,c	0.0001		OD+SE
	SD+ME	0.01±0.001a			SD+ME
	SD+SE	0.017±0.002c			SD+SE

Source: Authors, (2020).

Means ±SE of duplicate values with same alphabets are not significantly different; significant at p-value < 0.05.

Physico-Chemical Analysis

Specific gravity (SG): Result revealed no significant difference among the SG of oil samples which ranged between 0.73±0.09-0.91±0.06. This, however falls within fuel range (0.82-1.08) given by CSG [17] and also meets the ASTM [15] (0.87-0.90) standard for biodiesel production.

Fire point: Result revealed significant difference between the mechanically extracted oil and solvent extracted oil samples. Fire point for all samples ranged between 77.3±1.1-85.55 ±0.05 ºC and was observed to be lower than the required ASTM standard.

Viscosity: No significant difference was obtained among the viscosities of the samples. Result ranged between 4.05 ±0.55-4.45 ±0.15mm^2/sec, however, all samples fall within the standard range 2.5-6.0mm^2/sec given by ASTM/EN/IS 15607. This implies that the oil will have good fuel atomization and complete combustion and little or no carbon deposition.

Cloud point: The result obtained shows no significant difference among the oil samples. The cloud point obtained (7.25-8.35 ºC) fall within range (-3 to 12ºC) given by ASTM D6751. Oil samples of *H. barteri* gives good indication of a cold weather biodiesel feedstock.

Conradson carbon (CC): Values obtained shows that all samples have higher value of CC when compared to the maximum unit required by ASTM (0.05%). However, the result falls (0.15-0.28%) within same range with that of jathropha and rubber seed oil (0. 25%) and palm kernel oil (0.35%) (Oghenejoboh and Umukoro, 2014[18]).

Acid value (AV)/ Free-fatty acid (FFA): Result shows no significant difference among the AV and FFA values of the oil samples. Values obtained for all oil samples, was observed to be lower to the maximum value (0.50mgKOH/g) required by ASTM D6751 biodiesel standard. Low acid value is said to be an indicator for edibility of oil as well as their suitability for industrial use but a high acid value is only preferred in biofuels. Therefore, the AV result of the subject species proves its edibility as well as its possible use for green-fuel production.

Iodine value (IV): Result obtained which ranged between 57.95-61.85, was observed to be lower than the standard IV of 120 for biodiesel given by Europe's EN 14214 as cited by [19]. But according to B100Research, most oils and fats have an iodine value of between 44 and 75. Lower iodine value indicates that oil samples have lower degree of unsaturation and higher cloud point but good oxidative stability [20].

Calorific Value (CV): The range of CV obtained among the oil samples was 33.21-36.14MJ/kg. Though, values were observed to be lower when compared to the values obtained in some oil-bearing species such as corn oil and cottonseed oil (39.5MJ/kg), rapeseed oil (39.7MJ/kg), rubber seed oil (37.5 MJ/kg), soyabean oil and sunflower oil (39.6MJ/kg), crambe oil (40.5MJ/kg) and the petroleum diesel (43.8MJ/kg) [21] and [22]; jathropha seed oil (37.761MJ/kg) [18]. However, the result was found to be higher than the CV obtained in the studies of some biomass residues (14.43-16.20 kj/g or MJ/kg) [23]. The calorific or heating value obtained in this study indicates good combustion quality.

Table 4: Comparison of Physico-chemical properties with Biodiesel standard.

Properties	**Biodiesel Standard**	**Result for *H.barteri* oil**
Specific gravity	ASTM D6751 (0.880); ASTM 6751-02 (0.87-0.90)	0.73-0.91
Fire point	Not specified	77.30-84.55 ºC
Flash point	ASTM D6751 (93ºC)	44.35-45.95 ºC
Viscosity	ASTM/EN/IS15607-(2.5-6.0mm^2/sec)	4.05-4.45mm^2/sec
Cloud point	ASTM D6751-(-3 to 12ºC)	7.25-8.35 ºC
Conradson carbon	ASTM D6751 (0.05% max).	0.15-0.28%
Acid value	ASTM D6751 (0.50mgKOH/g)	0.032-0.034 mgKOH/g
Iodine value	EN14214 (120)	57.95-61.85
Calorific value		33.21-36.14MJ/kg

Source: Authors, (2020).

V. CONCLUSIONS

The study on the use of *H. barteri* fruit as a potential source of green-fuel or biodiesel meets almost all requirements for biodiesel production and the following conclusions could be drawn:

The solvent extraction method yielded more oil than the mechanical extraction method. From the elemental analysis, all elements except for carbon and hydrogen content are lower in the

oils samples while the sulphur content and the lower values of heavy metals obtained in this study compares favorably with the ASTM D6751 standard to an extent. The values obtained for specific gravity, viscosity, iodine value, cloud point conradson carbon residue from the physicochemical analysis indicate a good promising quality of biodiesel that will be produced from the oil of *H. barteri* fruit. The calorific values obtained in the oil samples with the highest as 36.14 MJ/kg indicate good combustion quality. Thus, the yield and physicochemical properties attest that *H. barteri* is an oil-bearing tree species suitable for both domestic and industrial applications. Hence, gives a basis for the exploitation of oil as a potential source for clean renewable biodiesel.

VI. AUTHOR'S CONTRIBUTION

Conceptualization: Adenike Evelyn Adeniyi and Abiodun Oluwafemi Oluwadare.
Methodology: Adenike Evelyn Adeniyi and Abiodun Oluwafemi Oluwadare.
Investigation: Adenike Evelyn Adeniyi.
Discussion of results: Adenike Evelyn Adeniyi.
Writing – Original Draft: Adenike Evelyn Adeniyi.
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Supervision: Abiodun Oluwafemi Oluwadare.
Approval of the final text: Adenike Evelyn Adeniyi and Abiodun Oluwafemi Oluwadare.

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