



Effects of Transesterification Variables on the Characteristics of the Methyl Esters Obtained from Four Virgin Tropical Seed Oils in Nigeria

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Authors' contributions

This work was carried out in collaboration between all authors. Author OGI designed the study, performed the experimental work, wrote the protocol, and wrote the first draft of the manuscript. Authors LL and MUO managed the analyses of the study, wrote a second draft and did some further literature search. Author SA managed the initial literature searches, author CAN is the overall supervisor of this research work. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

Four feedstock's comprising two inedible oils (*Telfaria occidentals* Hook F, (TVO) and *Hura crepitans* L (HVO)) and two edible oils (*Cucumeropsis manii* (CSVO) and *Canarium schweinfurthii* Engl.(CVO)) which are in abundance in the locality of study were investigated for production of biodiesel (methyl esters). Base catalysis was used for the transesterification reaction with methanol. The molar ratio oil/alcohol molar (4:1 and 6:1), catalyst type (KOH and NaOH), reaction time (5min and 30 mins) and reaction temperatures (38 and 55°C) were varied to achieve optimum yields of the biodiesel

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blends. The 6:1 generally showed better properties while the NaOH catalyst also showed better results. The 55°C summarily gave a better yield than the 38°C while the 30 mins contact time gave better results than 5 mins.

Keywords: Biodiesel; feedstock; catalyst; yield; transesterification; seed oil.

1. INTRODUCTION

Biodiesel is a renewable source of energy, non-toxic, biodegradable, and currently the best substitute for natural diesel today. Whatever source it may come from, the feedstock of biodiesel contains fats and oils that are liquid at room temperature. These fats or triglycerides are composed of carbon, hydrogen, and oxygen atoms bound together. Vegetable oils are potential biodiesel fuels possessing similar characteristic with fossil fuels but also having attendant difficulties due to higher viscosities and the poly-unsaturated nature of the bond structures. These are no doubt solvable with the recent development of biodiesel in the world. Process such as transesterification, pyrolysis or thermal cracking, micro-emulsification can be employed to produce biodiesel from vegetable oil with transesterification being the commonest and has been the first breakthrough for biodiesel production.

Nigeria's contribution to biodiesel production in the past has been very little, but research towards it has eventually just begun. At present, the emphasis is on biofuel/bioethanol production with the federal government's establishment of its plants and ethanol crop plantation across the country. In fact, within the last few years, the Nigerian government has seen the need to de-emphasis the total dependence on petroleum based fuels [1].

Properties and characteristics of biodiesel before and after transesterification are important considerations as far as using vegetable oils as feedstock for biodiesel production is concerned. The ASTM system is the basis for defining product specification and measurement methods for most segments of the fuels and industrial products market in the U.S. ASTM D6757-09 sets forth the specification that must be met for a fatty acid ester product to carry the designation 'biodiesel fuel' or 'B100'. Products that meet the specification, by implication, will perform properly as a compression ignition fuel either as B100 or in blends with any petroleum derived diesel fuel defined by ASTM specification D975 Grades 1-D, 2-D and low sulphur 1-D and 2-D. [2]. The values of the various biodiesel properties specified by ASTM D6751 are listed in Table 1.

Since the properties of the biodiesel produced are very important to its quality for efficient use, we set out to prepare, characterize and studied biodiesel properties by transesterification, varying conditions of molar ratio, temperature, contact time and catalyst type for four feedstock (methyl esters) comprising two inedible oils (*Telferia occidentals* Hook F, (TVO) and *Hura crepitans* L (HVO)) and two edible oils (*Cucumeropsis manii* (CSVO) and *Canarium schweinfurthii* Engl.(CVO) to check their % Yield , Viscosity, Specific Gravity, cloud point, flash point etc.

Table 1. ASTM D6751-09 standards for biodiesel

Property	Method	Limits	Units
Flash point. Closed cup	D93	130min	°C
Water and sediment	D2709	0.050max	%volume
Kinematic viscosity 40°C	D445	1.9-6.0	Mm ² /s
Sulphated ash	D874	0.020max	Wt%
Total ash	D5454	0.050max	Wt%
Copper strip corrosion	D130	No.3max	
Cetane number	D613	47min	
Cloud point	D2500	Report	°C
Carbon residue	D4530	0.050max	Wt%
Acid number	D664	0.80max	mgKOH/g
Free glycerine	D6584	0.020max	Wt%
Total glycerine	D6584	0.240max	Wt%
Phosphorus	D4951	0.0010	Wt%
Vacuum distillation end point	D1160	360°Cmax	°C
Oxidative stability	EN14538	At 90% 5max	ppm
Sodium/potassium	EN14538	3min	hours
Calcium, magnesium	EN14538	5max	ppm

2. MATERIALS AND METHODS

2.1 Test Materials/Sample Collection

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 [3] have reported 22 – 27% oil yield for the seed. These 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 used for extraction.

Hura crepitans is the large forest tree often found in the tropical rain forest and Savanna regions of Nigeria. The seeds are enclosed in a 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. This seed has been reported to yield 37.75 ± 0.40% oil [4]. The seeds were collected from Makurdi metropolis during the dry season, sun dried to remove moisture after which it was crushed and milled.

Telfaria occidentalis belongs to the family *Cucurbitaceae* spp. It is popularly known locally as 'Ugu' among the Igbo, Idoma and Tiv people of north central and the Igbos of eastern 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 *Cucurbitaceae* extends to both vegetative and reproductive characteristics. *Telfaria occidentalis* has become an important medicine source in the last decades. It has been reported in the literature to give oil yield of about 45% [5]. The seeds were obtained from Wurukum market, in Makurdi Local Government of Benue State (north central Nigeria) between December and January. 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.

Cucumeropsis manii (white melon) is one of the species of melon commonly found everywhere in Nigeria. The seeds are edible and are usually used in preparation of soup among the different ethnic nationalities. The seeds were gotten from Oju Local Government of Benue State during the dry season and were dried to a constant weight; the mesocarps were removed while the seeds were milled into a coarse powder and ready for extraction. Recent research shows that oils from these seeds stated above have previously been considered as economical for commercial production of oil in Nigeria [6].

2.2 Degumming of Crude Oils

The oils were degummed to remove phospholipids, calcium and magnesium salts of phosphatidic and lysophosphatidic 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°C. This hydrates the phospholipids and gums thus making them insoluble in the oil. They were thereafter separated by settling.

2.3 Physiochemical Analysis

Determination of free fatty acid value, iodine value, moisture content (oven method), saponification value, kinematic viscosity, specific gravity and peroxide value were carried.

2.4 Production of Biodiesel Fuels

A quantity (100 mL) of the oil was measured and poured into a large beaker. Pretreatment by heating the oil to a temperature of 70°C using a Bunsen burner to remove the remaining solvent or moisture content. Prior to transesterification, sodium hydroxide was added to methanol and mixed thoroughly in a blender to form sodium methoxide (catalyst). The mixture was immediately transferred and mixed with the methoxide at a molar ratio of 6:1 or 4:1 as applicable in a 250 mL spherical flask equipped with reflux condenser, magnetic stirrer/heater and was stirred [7]. The mixture was allowed to settle for 24 h in a separating funnel after which a dark color glycerin settled at the bottom while a pale liquid layer which is the methyl ester separated at the top [8].

2.5 Biodiesel Separation

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

2.6 Biodiesel Washing

The methyl ester 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 was drained off from the bottom of the funnel by turning on the tap of the separating funnel. The tap was turned off when it reaches the methyl ester. This procedure was repeated twice to ensure complete washing. After washing, the methyl ester was dried by heating [9].

ASTM quality evaluation/Physiochemical analysis of methyl esters derived biodiesel oils were carried out as enumerated; Tat et al [10]; Sims[11]; Ayhan[12]; ASTM [13]; ASTM [14]; Horwitz and Latimer [15]; Kirk,[15]; IUPAC[17]; IPMAN [18]; Chevron Corporation [19]; Lewkowitsch [20]; AOC International [21]; Sanger and Black [22]; and Tat and Van Gerpen [23]

- Determination of the Kinematic viscosity (ASTM D 445).
- Density/Specific gravity (ASTM D 4052/ISO-AOAC Method).
- Determination of flash point (ASTM D93).
- Determination of pour point (ASTM D97 Method).
- Determination of cloud point (ASTM D97 Method).
- ASTM D 2709 Standard Test Method for Water and Sediment in Middle Distillate fuels by Centrifuge (Biodiesel limit – 0.05 volume %).
- Determination of carbon residue (ASTM D189 method).
- Free Glycerin and Total Glycerin.
- For biodiesel, GC forms the basics of the standard ASTM D6584.
- ASTM D – 874: Standard Test Method for Sulfated Ash from Lubricating Oils and Additives (Biodiesel limit – 0.02 mass %).
- ASTM D515. Determination of Phosphorus (Perkin Elmer Lambda 2UV/VIS Spectrometer Manuel)
- ASTM D – 7039: Standard Test Method for Determination of Sulfur in gasoline, and diesel fuel by Monochromatic Wavelength Dispersive X-ray Fluorescence spectrometry (Biodiesel limit – 0.05 mass %)
- Refractive Index (n) was determined using Abbe Refractometer.

3. RESULTS

Table 2 - 5 shows the different feedstocks, transesterification variables, yields, viscosities and specific gravities. While Tables 6 - 9 shows their corresponding characteristics as illustrated serially respectively. These tables also show the various sample descriptions.

4. DISCUSSION

4.1 Effects of Molar Ratio on Characteristics

TVO-ME: Increase in viscosity was also related to increase in water and sediments with 6:1 giving better results with water and sediment been within specification. Flash point had higher value with 4:1 molar ratio than 6:1. From Table 6, samples 9, 10 and 12 had flash point lower than AGO; this may be due to excess methanol present which may not be completely removed during the washing. All the cloud points have higher values ranging from $> +7 < +14$ with 4:1 possessing the highest. Pour point also follows a similar trend with 6:1 having lower values of +3 and +4. Phosphorus, total glycerine, free glycerine, acid value and refractive index showed no significant variations as they all fall within limits of specification. Similar effects of these variables on these properties have been earlier reported Igbum et al. [24, 25].

Total sulphur was measured in % wt and was absent in all cases, compared to AGO with 0.310wt%. Carbon residue and sulphated ash were all within specification with no significant variation between the two alcohol/oil molar ratios used.

Table 2. Yields, viscosity and specific gravity of methyl esters (Biodiesel) from *Telfaria occidentalis* seed oil (TVO-ME) at varied conditions

S/No.	Feedstock	Catalyst	Catalyst conc. (%)	Alcohol/Oil ratio	Retention temp. (°C)	Rxn time (mins)	% Yield	Viscosity mm ² /s	Specific gravity g/cm ³
1	TVO-ME	KOH	1	4:1	38	5	94	6.40	0.90
2	TVO-ME	KOH	1	4:1	55	5	94.5	5.50	0.90
3	TVO-ME	KOH	1	4:1	38	30	94	6.21	0.90
4	TVO-ME	KOH	1	4:1	55	30	93	5.22	0.89
5	TVO-ME	NaOH	1	4:1	38	5	8	8.30	0.99
6	TVO-ME	NaOH	1	4:1	55	5	8	7.80	0.99
7	TVO-ME	NaOH	1	4:1	38	30	9	8.01	0.99
8	TVO-ME	NaOH	1	4:1	55	30	9	7.40	0.99
9	TVO-ME	KOH	1	6:1	38	5	92	4.01	0.87
10	TVO-ME	KOH	1	6:1	55	5	94	6.20	0.88
11	TVO-ME	KOH	1	6:1	38	30	93	4.80	0.89
12	TVO-ME	KOH	1	6:1	55	30	93	4.30	0.87
13	TVO-ME	NaOH	1	6:1	38	5	97	3.91	0.87
14	TVO-ME	NaOH	1	6:1	55	5	97	4.12	0.87
15	TVO-ME	NaOH	1	6:1	38	30	85	4.02	0.87
16	TVO-ME	NaOH	1	6:1	55	30	87	4.20	0.87
17	AGO							1.62	0.96

Table 3. Yields, viscosity and specific gravity of methyl esters (Biodiesel) from *Hura crepitans* seed oil (HVO-ME) at varied conditions

S/No.	Feedstock	Catalyst	Catalyst conc. (%)	Alcohol /Oil ratio	Retention temp. (°C)	Rxn time (mins)	% Yield	Viscosity mm ² /s	Specific gravity g/cm ³
1	HVO-ME	KOH	1	4:1	38	5	80	19.50	0.91
2	HVO-ME	KOH	1	4:1	55	5	92	22.0	0.96
3	HVO-ME	KOH	1	4:1	38	30	90	17.32	0.90
4	HVO-ME	KOH	1	4:1	55	30	90	17.30	0.90
5	HVO-ME	NaOH	1	4:1	38	5	59	4.60	0.88
6	HVO-ME	NaOH	1	4:1	55	5	9	4.20	0.87
7	HVO-ME	NaOH	1	4:1	38	30	58	4.23	0.87
8	HVO-ME	NaOH	1	4:1	55	30	62	4.00	0.87
9	HVO-ME	KOH	1	6:1	38	5	88	6.40	0.90
10	HVO-ME	KOH	1	6:1	55	5	70	17.90	0.91
11	HVO-ME	KOH	1	6:1	38	30	92	18.51	0.91
12	HVO-ME	KOH	1	6:1	55	30	83	16.61	0.90
13	HVO-ME	NaOH	1	6:1	38	5	97	5.02	0.88
14	HVO-ME	NaOH	1	6:1	55	5	90	4.20	0.87
15	HVO-ME	NaOH	1	6:1	38	30	72	3.60	0.87
16	HVO-ME	NaOH	1	6:1	55	30	85	4.02	0.87
17	AGO							1.62	0.96

Table 4. Yields, viscosity and specific gravity of methyl esters (Biodiesel) from *Cucumeropsis manii* seed oil (CVO-ME) at varied conditions

S/No.	Feedstock	Catalyst	Catalyst Conc. (%)	Alcohol /Oil Ratio	Retention temp. (°C)	Rxn time (mins)	% Yield	Viscosity mm ² /s	Specific gravity g/cm ³
1	CVO-ME	KOH	1	4:1	38	5	T G	H V	-
2	CVO-ME	KOH	1	4:1	55	5	T G	H V	-
3	CVO-ME	KOH	1	4:1	38	30	T G	H V	-
4	CVO-ME	KOH	1	4:1	55	30	T G	H V	-
5	CVO-ME	NaOH	1	4:1	38	5	T G	H V	-
6	CVO-ME	NaOH	1	4:1	55	5	T G	H V	-
7	CVO-ME	NaOH	1	4:1	38	30	T G	H V	-
8	CVO-ME	NaOH	1	4:1	55	30	T G	H V	-
9	CVO-ME	KOH	1	6:1	38	5	T G	H V	1.26
10	CVO-ME	KOH	1	6:1	55	5	T G	H V	1.26
11	CVO-ME	KOH	1	6:1	38	30	T G	H V	1.24
12	CVO-ME	KOH	1	6:1	55	30	T G	H V	1.20
13	CVO-ME	NaOH	1	6:1	38	5	T G	H V	1.12
14	CVO-ME	NaOH	1	6:1	55	5	T G	H V	1.12
15	CVO-ME	NaOH	1	6:1	38	30	T G	H V	1.14
16	CVO-ME	NaOH	1	6:1	55	30	T G	H V	1.12
17	AGO							1.62	0.96

Table 5. Yields, viscosity and specific gravity of methyl esters (Biodiesel) from *Canarium schweinfurthii* seed oil (CSVO-ME) at varied conditions

S/No.	Feedstock	Catalyst	Catalyst conc. (%)	Alcohol /Oil ratio	Retention temp. (°C)	Rxn time (mins)	% Yield	Viscosity mm ² /s	Specific gravity g/cm ³
1	CSVO-ME	KOH	1	4:1	38	5	74	5.82	0.90
2	CSVO-ME	KOH	1	4:1	55	5	82	3.60	0.87
3	CSVO-ME	KOH	1	4:1	38	30	83	3.83	0.87
4	CSVO-ME	KOH	1	4:1	55	30	85	4.02	0.87
5	CSVO-ME	NaOH	1	4:1	38	5	9	4.20	0.87
6	CSVO-ME	NaOH	1	4:1	55	5	9	4.10	0.87
7	CSVO-ME	NaOH	1	4:1	38	30	9	4.60	0.88
8	CSVO-ME	NaOH	1	4:1	55	30	9	4.11	0.87
9	CSVO-ME	KOH	1	6:1	38	5	94	4.51	0.88
10	CSVO-ME	KOH	1	6:1	55	5	93	4.22	0.88
11	CSVO-ME	KOH	1	6:1	38	30	83	4.40	0.88
12	CSVO-ME	KOH	1	6:1	55	30	82	4.91	0.89
13	CSVO-ME	NaOH	1	6:1	38	5	7	4.82	0.88
14	CSVO-ME	NaOH	1	6:1	55	5	8	4.60	0.87
15	CSVO-ME	NaOH	1	6:1	38	30	8	4.41	0.87
16	CSVO-ME	NaOH	1	6:1	55	30	7	4.60	0.87
17	AGO							1.62	0.96

Table 6. Characteristics of methyl esters of *Telfaria occidentalis* seed oil

S/No.	Water & sediments (%)	Flash point (°C)	Cloud point (°C)	Pour point (°C)	Phosphorus	Total glycerine	Free glycerine	Acid Value	Sulphur content (%wt)	Refractive index	Carbon residue	Sulphated ash
1	0.15	168	+14	+7	0.009	0.106	0.006	0.374	Nil	1.467	0.014	0.007
2	0.10	167	+14	+7	0.009	0.104	0.003	0.374	Nil	1.467	0.016	0.006
3	0.25	167	+14	+7	0.009	0.106	0.006	0.374	Nil	1.467	0.017	0.006
4	0.10	166	+14	+7	0.009	0.104	0.006	0.374	Nil	1.467	0.016	0.005
5	-	-	-	-	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-	-	-
9	0.10	118	+8	+3	0.009	0.112	0.005	0.374	Nil	1.457	0.012	0.006
10	0.25	121	+12	+3	0.009	0.106	0.004	0.374	Nil	1.457	0.022	0.005
11	0.05	132	+8	+3	0.009	0.102	0.004	0.374	Nil	1.457	0.012	0.006
12	0.05	121	+8	+3	0.009	0.106	0.004	0.374	Nil	1.457	0.021	0.006
13	<0.05	134	+11	+4	0.009	0.106	0.004	0.374	Nil	1.456	0.023	0.005
14	<0.05	134	+11	+4	0.009	0.103	0.003	0.374	Nil	1.456	0.025	0.02
15	0.05	132	+7	+4	0.009	0.089	0.003	0.374	Nil	1.456	0.022	0.017
16	0.05	134	+8	+4	0.009	0.125	0.008	0.374	Nil	1.456	0.021	0.006
17	0.05	128	Nil	<2	0.189				0.0310	1.471	0.035	0.006

Table 7. Characteristics of methyl esters of *Hura crepitans* seed oil

S/No.	Water & Sediments (%)	Flash point (°C)	Cloud point (°C)	Pour point (°C)	Phosphorus	Total glycerine	Free glycerine	Acid Value	Sulphur content (%wt)	Refractive Index	Carbon residue	Sulphated ash
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	0.10	148	+1	-4	Nil	0.129	0.006	0.561	Nil	1.466	0.016	0.004
6	0.10	142	+1	-6	Nil	0.129	0.009	0.561	Nil	1.461	0.016	0.005
7	0.05	148	+1	-4	Nil	0.126	0.006	0.561	Nil	1.467	0.017	0.006
8	0.10	146	+1	-4	Nil	0.141	0.005	0.561	Nil	1.467	0.014	0.004
9	-	-	-	-	-	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-	-	-	-	-	-
13	0.05	136	0	-9	Nil	0.108	0.005	0.560	Nil	1.467	0.019	0.01
14	<0.05	134	0	-9	Nil	0.107	0.002	0.560	Nil	1.452	0.014	0.007
15	<0.05	126	+4	-6	Nil	0.124	0.006	0.560	Nil	1.452	0.017	0.006
16	<0.05	130	+4	-3	Nil	0.124	0.007	0.560	Nil	1.451	0.013	0.006
17	0.05	128	Nil	≤23	0.189				0.0310	1.471	0.035	0.006

Table 8. Characteristics of methyl esters of *Canarium schweinfurthii* seed oil

S/No.	Water & sediments (%)	Flash Point (°C)	Cloud Point (°C)	Pour Point (°C)	Phosphorus	Total glycerine	Free glycerine	Acid Value	Sulphur Content (%wt)	Refractive Index	Carbon residue	Sulphated ash
1	0.15	119	+11	+4	Nil	0.121	0.009	0.468	Nil	1.410	0.012	0.010
2	<0.05	118	+11	+3	Nil	0.120	0.006	0.468	Nil	1.453	0.013	0.006
3	<0.05	118	+11	+3	Nil	0.119	0.008	0.468	Nil	1.452	0.012	0.006
4	<0.05	118	+11	+4	Nil	0.121	0.009	0.468	Nil	1.451	0.014	0.006
5	-	-	-	-	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-	-	-
9	0.05	141	+11	+4	Nil	0.121	0.010	0.468	Nil	1.452	0.036	0.008
10	0.05	140	+11	+3	Nil	0.121	0.009	0.468	Nil	1.452	0.039	0.008
11	0.05	139	+11	+3	Nil	0.118	0.008	0.468	Nil	1.453	0.035	0.007
12	0.05	141	+11	+3	Nil	0.120	0.009	0.468	Nil	1.453	0.029	0.009
13	-	-	-	-	-	-	-	-	-	-	-	-
14	-	-	-	-	-	-	-	-	-	-	-	-
15	-	-	-	-	-	-	-	-	-	-	-	-
16	-	-	-	-	-	-	-	-	-	-	-	-
17	0.05	128	Nil	≤23	0.189	-	-	-	0.0310	1.471	0.035	0.006

Table 9. Characteristics of methyl esters of *Cucumeropsis manii* vegetable oil

S/No.	Water & sediments (%)	Flash point (°C)	Cloud point (°C)	Pour point (°C)	Phosphorus	Total glycerine	Free glycerine	Acid Value	Sulphur content (%wt)	Refractive index	Carbon residue	Sulphated ash
1	.	.	.	.	.	.	.	.	.	.	.	.
2	.	.	.	.	.	.	.	.	.	.	.	.
3	.	.	.	.	.	.	.	.	.	.	.	.
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16	.	.	.	.	.	.	.	.	.	.	.	.
17	0.05	128	Nil	<23	0.189	NA	NA	NA	0.0310	1.471	0.035	0.006
18	<0.05	137	+11	+4	Nil	0.119	0.006	0.468	Nil	1.452	0.020	0.020
19	<0.05	129	+10	+4	Nil	0.139	0.006	0.468	Nil	1.450	0.023	0.006
20	<0.05	130	+11	+4	Nil	0.120	0.006	0.468	Nil	1.452	0.020	0.02
21	<0.05	136	+11	+4	Nil	0.128	0.006	0.468	Nil	1.453	0.021	0.02
22	<0.05	121	+8	+4	Nil	0.097	0.007	0.468	Nil	1.456	0.044	0.02
23	<0.05	119	+8	+4	Nil	0.099	0.007	0.468	Nil	1.456	0.047	0.03
24	<0.05	119	+10	+4	Nil	0.099	0.007	0.468	Nil	1.456	0.049	0.02
25	<0.05	120	+11	+6	Nil	0.102	0.006	0.468	Nil	1.456	0.046	0.02

HVO-ME: Water and sediment was out of specification for 4:1 molar ratio but within specification for 6:1 molar ratio. Flash point gave higher values for 4:1 and value for 6:1 which is lower than 4:1 but within specification as shown in Table 7. Sample 15 has flash point lower than that of AGO studied. Cloud points are reasonably low and lowest at 4:1 molar ratios ($> +1 < +1$) and best at 6:1 (sample 14). Pour points remarkably impressive and lowest at 6:1 (sample 14). Phosphorus and total sulphur were found to be absent in all samples. Total glycerine was lowest at 6:1 (sample 14) but all values are within specifications. Free glycerine was also within specification and lowest at 6:1 (sample 14). Acid value and refractive index did not show significant variation for all samples studied.

CSVO-ME: Table 8 shows the results of the characteristics of CSVO-ME. Water and sediment showed no significant variation except for sample (1). Flash point lowest at 4:1 within the range of 118 – 119°C, which is quite lower than for AGO (128°C). Cloud points were quite high (+11°C) for all samples and pour points were within the range of +3 - +4°C for all samples. Total glycerol, free glycerine, acid value and refractive index showed no significant variation. CSVO-ME was found to form soap on prolonged storage.

CVO-ME: Effect of molar ratio does not apply when a molar ratio of 4:1 and 6:1 were used, the oil form glycerol completely by the end of the methanolysis reaction. An excess methanol in a molar ratio of 9:1 was then introduced and observed. Samples with KOH, NaOH gave water and sediment values within specification. Flash point were best for KOH catalyst (129 - 137°C) than NaOH (119 – 121°C). Cloud points were lowest in sample 22 and 23; and the order ranges from +10 - +11°C. Pour point showed no significant variation except for sample 25 with +6°C. Phosphorus and sulphur content was nil. Free glycerine showed no significant variation. Total glycerine was lower for NaOH catalyst ranging from 0.097 – 0.102 than KOH which ranged from 0.119 – 0.139 but all were within specification. Acid number showed no significant difference as showed in Table 9.

4.2 Effect of Catalyst Type on the Characteristics of the Methyl Esters

TVO-ME: The results are showed in Table 6. Water and Sediment for KOH samples were off specification, while NaOH were within specification. The trend for flash point is inconsistent with catalyst type because at 6:1 molar ratio, KOH seems to give lower values (118 – 132°C) compared to the higher values (166 – 168°C) obtained for KOH for 4:1 molar ratio, these the effect may be more or less due to molar ratio than catalyst type. Cloud point was also inconsistent with regard to catalyst type because of the same reason given in the case of flash point. The pour point also follows the same trend. Phosphorus, acid number, sulphur refractive index, total and free glycerine also show inconsequential trends that note that these properties are not affected by catalyst type.

HVO-ME: Effect of catalyst type does arise because only one catalyst NaOH was effective in the transesterification reaction as shown in Table 7. When KOH was used the methyl ester obtained had very high viscosities ranging from 6:02 mm/s² – 22.0 mm/s²; which is out of specification. Therefore, such methyl ester cannot be considered to be used as biodiesel.

CSVO-ME: Effect of catalyst type does not play a role in the characteristics of the methyl esters as well. This is because only KOH favour the methanolysis of these oils. Very low yields (7 – 9%) were observed when NaOH was used in the methanolysis reaction. Refer to Table 8.

CVO-ME: The effect of catalyst type did not apply to the following properties, water and sediments, cloud point, pour point, phosphorus, acid value, sulphur content, refractive index, total glycerol because their results show no significant difference as shown in Table 9. The flash point was better enhanced with KOH ranging from 129 – 137°C, while flash point for NaOH samples ranged from 119 – 121°C. Also total glycerin for samples with KOH ranged from 0.119 – 0.139 while NaOH ranged from 0.097 – 0.102 also shown on the same table.

5. CONCLUSION

TVO-ME exhibited better results in water and sediment, pour points. 4:1 alcohol/oil molar ratio showed higher flash points, while the rest of properties, showed no significant variation as they all fall within limits of specification. HVO-ME exhibited better properties at 6:1 ratio for all properties tested for. CSVO-ME gave higher flash point at 6:1 alcohol molar ratio (139-141°C) compared to 4:1 (118-119°C). CVO-ME had flash point which were best for KOH catalyst (129-137°C) than NaOH (119-121°C). Total glycerin values were lower (0.097-0.102) for NaOH than KOH (0.119-0.139) but all were within specification. Effect of catalyst type does arise for HVO-ME and CSVO-ME, when looking at the properties since only one catalyst was able to transesterify the oils i.e NaOH for HVO-ME and KOH for CSVO-ME. Therefore TVO-ME, HVO-ME CVO-ME and CSVO-ME can be recommended for biodiesel production, even though longer storage time for CVO-ME and CSVO-ME may poses a challenge which can be enhanced by use of additives.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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