An Investigation into the Biodiesel Properties of Oil Extracted from Three Papaya Cultivars

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***Abstract*: The trends in energy researches in recent time toward conversion of agricultural residues into useful products so as to solve the problem of climate change and encourage green energy. Pawpaw seed being one of the agricultural residues usually discarded after consumption of its fruit was investigated to study the biodiesel properties of its oil. Three cultivars (solo, maradol and js 22) of ripe pawpaw seeds were used for the research. The three cultivars were obtained from a retail outlet in Ado Ekiti. The seeds were collected, sun dried for five days and dried in an oven at 60 °C for six hours. The dried seeds were milled and oil was extracted using 30 g of milled seeds using solvent method with the aid of soxhlet extractor. The oil yield, specific gravity, free fatty acid, iodine value, saponification value, peroxide value and refractive index were the parameters investigated for biodiesel properties. The result shows that the oil yield is higher with 28, 23 and 23% for maradol, solo and js 22 respectively, although the values are low as compared to other sources of vegetable oil. The specific gravity, iodine value, saponification value, peroxide value, refractive index and free fatty acid value of the oil from the three cultivars are within the range of values for biodiesel production when compared to other oils used as feedstock for biodiesel. The oil from the three cultivars is therefore recommended for biodiesel production.**

***Keywords*: cultivar, pawpaw seed, oil, biodiesel.**

I. INTRODUCTION

Fossil fuel is the main energy source which is consumed worldwide and has been in use for decades which has been causing major problems for mankind and his environment (Agunbiade and Adewole, 2014). Some of these problems are fuel scarcity which has led to a fluctuation in price, depletion of the ozone layer by an increased level of green gas emission, destruction of farmlands and water bodies etc. Thus, the need for an energy source which is renewable is required from biological materials. One of such natural biological materials is the use of biodiesel.

Biodiesel consists of variety of ester-based oxygenated fuels gotten from vegetable oil, seed oil, animal fats, tallow etc. through a process termed transesterification. Vegetable oils are used as fuel by converting into biodiesel through alcoholysis process. This process helps in fuel properties improvement by lowering the viscosity and increasing the volatility of the vegetable oil (Encinar *et al.*, 2002 and Arthe *et al.*, 2008).

Recently, the conventional source material for biodiesel production is gotten from oil seeds that are fit for human consumption like rapeseed, soybean, canola, sunflower, palm, coconut pawpaw and corn oil. However, this practice could lead to food insecurity as most of these biomaterials are food source hence, there will be competition (Al *et al*., 2008). In order not to compromise the food industry, non-edible oil (pawpaw seed oil) had been used as raw material for manufacturing biodiesel (Arthe *et al*., 2008).

Carica papaya as a major fruit crops has an annual production of over 10 million tons (Scheldeman *et al.*, 2011). Medina *et al.* (2003) stated that the fruit pulp of pawpaw is consumed by man, the foliage is used in the production of fish feed and its seed oil is used in cosmetics product. Also, the seeds of pawpaw have depicted to be a provenance of oil which is needed for medicinal, biofuel and industrial purposes (Afolabi *et al*., 2011). These uses of pawpaw depend on the different varieties of pawpaw which differ in their shape, size, form, and color; this is as a result of its complex genetic makeup. There are few true cultivars of pawpaw which has uniform characteristics as the cultivars of other herbaceous crops (Morton, 2007). According to Scheldeman *et al.* (2011), some of the recognized cultivars of pawpaw are solo, mountain pawpaw, maradol, js.22 and babaco.

Sharma and Singh (2010) and Robles *et al.* (2009), opined that the various factors to consider for crude oil for biodiesel are a fatty acid, saponification value, oil percentage and yield per hectare, viscosity, iodine value, flash point, pour point, peroxide value etc. According to Fariku *et al* (2007), Eka *et al*. (2010) and Adnan *et al*. (2009) opined that the aptness of biodiesel fuel can be indicated from density, saponification value, iodine value, heating value and specific gravity of the vegetable oil source.

Presently, the prevalent methods used for the retrieving of oil from natural products are extrusion, expelling extraction, soxhlet solvent extraction and aqueous enzymatic extraction (Li *et al*., 2015).

Researcher such as Malacrida *et al.* (2010), Li *et al.* (2015), Kalou *et al*. (2011), Syed *et al.* (2012) had done a lot of researches on characterization of papaya seeds in the production of biodiesel but there is no report on extraction of oil using different cultivar of pawpaw for biodiesel production. Thus, this research work investigates biodiesel properties of oil extracted from three cultivars of pawpaw seed.

II. MATERIALS AND METHODS

2.1 Materials

Ado Ekiti is a city in Southwest Nigeria, situated within the tropics and located between longitudes 4°5' and 5° 45' and latitudes 7° 15' and 8° 5' on the East and North of the Greenwich meridian respectively. The state is buoyant in agricultural terms with cocoa, timber, yam; varieties of fruits etc. are cultivated in commercial quantities. Papaya has reported by Ajayi and Kayode (2020) has the highest number of species in an urban community in Ekiti state, with maradol, Js22 and solo being the highest cultivar. The three cultivars of pawpaw were obtained from the retail markets in Ado Ekiti in Nigeria. The seeds were taken out from the fruits by carefully cutting the fruits longitudinal into two halves with sharp knife to extract the seed. The paste was brought out by washing the seeds gently in distilled water. The cleaned seeds were sun dried for 5 days; oven dried at 60 °C for proper drying and milled using kitchen blender of model no QBL-15L40. The milled samples were enclosed in a black polymer bag, sealed and stored at room temperature for further processing.

2.2 Methods

2.2.1 Oil extraction

Oils from seeds were extracted by using solvent extraction method in accordance with procedures of Oyedele and Ogunnaike (2018). 100g of each milled powdered seed sample was wrapped with filter paper and inserted in a porous thimble of a soxhlet extractor. This was mounted on a round bottom flask containing 333ml of n-hexane (solvent) and placed on the heating mantle. The temperature of heating mantle was set at 150°C after the whole arrangements have been connected to water circulator. The extraction of oil occurs as the solvent (n-hexane) boils and evaporate and condense at the porous thimble where the wrapped paper was placed. The solvent wash down the oil into the flask and the process continues for 8 hours. The filtrate which was collected after the solvent had siphoned over the barrel, was kept in a desiccator and cooled at room temperature. The oil extracted was separated by re-heating of the mixture of oil and n-hexane. Figure 2.1 shows the flow chart of process involved in extraction of oil from papaya seeds.

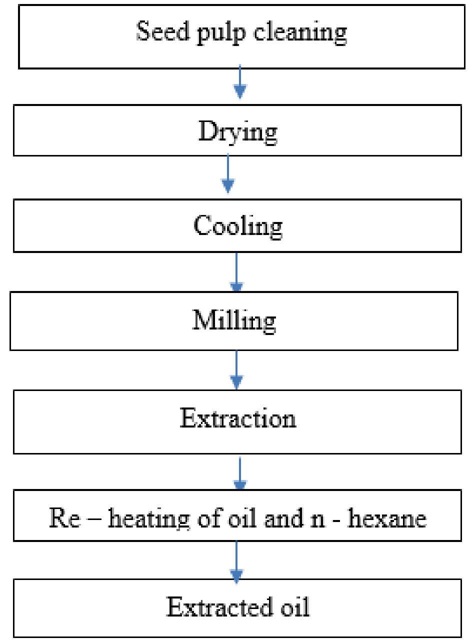

Figure 2.1: Flow chart of process involved in extraction of oil from papaya seeds.

2.2.2 Description of the Extracted Oil

2.2.2.1 Oil yield determination

The oil yield was determined using the method proposed by Oyedele and Ogunnaike (2018). The oil content was calculated using equation (1) (Ardabili *et al*., 2011).

$$Oil\ content = \frac{Weight\ of\ oil}{Weight\ of\ sample}\ X\ 100 \qquad (1)$$

2.2.2.2 Iodine value

The iodine value was determined in accordance with the method of AOAC (2002). The iodine valve was computed using equation (2)

$$Iodine\ value\ (IV) = \frac{(A-N)\ X\ Y\ X\ 12.69}{r} \qquad (2)$$

Where A is blank titre value, N is sample titre value, Y is molarity and r is weight of oil.

2.2.2.3 Refractive index of the oil

Refractive index was determined using the method of procedures used and reported by Ibanga (2014). A drop of the sample was introduced on the working surface of the lower refracting prism. The rotating arm and the collecting lens cone of the light gathering illuminating unit were rotated so as to make the light – intake surface of the upper light- intake prism to be illuminated evenly. The field of view was observed through the eyepiece and adjustable hand wheel was rotated so as to make the line dividing dark and light areas fall in the cross line. The dispersion correction hand wheel was rotated so as to get the good contrast between the light and dark area and minimum dispersion. The red button was then pressed and the refractive index was displayed on the screen.

2.2.2.4 Determination of acid value

Acid value of the oil was determined using the method of AOAC (2002). The acidic value is calculated using equation (3) as reported by Akintayo and Bayer (2012).

Acid Value $= \frac{P\ X O\ X\ 56.1}{K}$ (3)

Where P is volume of ethanolic KOH used, O ismolarity of ethanolic KOH used and K is weight of oil.

2.2.2.5 Saponification value Determination

Saponification value of the oil was determined using the method of Balaimi *et al*. (2004). The saponification value of the oil was calculated using the relationship as proposed by Akanni, *et al*. (2005).

Saponification (SV) $= \frac{(Z-D)\ X\ \ V\ X\ 56.1}{L}$ (4)

Where Z is titre value of the sample, D is titre value of blank, V is molarity of H_2SO_4 and 56.1 is molecular weight of KOH. L is the weight of oil.

2.2.2.6 Determination of peroxide value

Peroxide value of the oil was determined using the method of AOAC (2002). The peroxide value of the oil was calculated using the relationship (equation 5) as given by AOAC (2002).

Peroxide value (PV) $= \frac{(Z-D)\ X\ 1000}{L}$ (5)

Where Z is titre value of sample, D is blank titre value, , and W is weight of the oil.

2.2.2.7 Determination of cloud point

The cloud point was determined by visual observation of cloudiness at the bottom of the glass jar placed in a refrigerator. The temperature of the sample was read by a digital thermometer placed at the bottom jar.

2.2.2.8 Determination pour point

The pour point was ascertained on the oil by keeping the extracted oil in a refrigerator. The temperature at which the oil doesn't flow when tilted within five seconds was determined. The pour point was determined when there was no temperature movement.

III. RESULTS AND DISCUSSION

Table 1.1 reveals the extracted oil properties while Table 1.2 depicts comparison of the extracted oil with other seed oils and ASTM standards.

3.1 Oil yield

Table 1.1 depicts the oil yield from three cultivars of pawpaw seed oil. Oil yield of 27.98%, 22.58% and 22.52% are obtained for maradol, js. 22 and solo respectively. These values do not fall within the recommended range of 30 - 55% for industrial oil production for diesel. Although the quantity of oil gotten from each cultivar was higher than oil yield of desert melon (19 – 21%), cotton seed (15 – 20%) and "sesoswane" (24%) as reported by Bwade *et al*. (2013).Oil yields from js. 22 and solo cultivars are in close range with that obtained from cotton seed (22.9%), tiger nut (22.10% when dried at 60 ºC) (Oyedele and Ogunnaike, 2018) but greater than that obtained from soya beans (21%) and corn oil (4.5%). Notwithstanding, the quantity of oil yield from the three cultivars are small when compared with oil yield of groundnut (47.2%), safflower (30.5) and jatropha seed (Azam *et al.*, 2005; Shah and Gupta 2009). This reveals that the quantity of oil in the samples cannot be recommended for industrial production of biodiesel.

3.2 Free fatty acid

The amount of free fatty acids in the raw oil for biodiesel production is a major factor in reaction of biodiesel. Free fatty acids affect the wastage of oil if it is high. The values of fatty acid (Table 1) obtained from the three papaya cultivars were compared with various seeds oil that were used for producing biodiesel. The values of 0.514%, 0.499% and 0.496% of fatty acid were obtained from maradol, js 22 and solo respectively. Comparing these values with those on Table 2, the fatty acid values were the same with that of safflower and soya bean oil (0.4% and 0.5% respectively), although, the values were far lower than those of groundnut (3.01%) and melon (2.38%). From Table 2, the values obtained meets with the ASTM standard since the reaction from transesterification can take less than1 percent of free fatty acid amount and less than 0.5 percent is not significant. For Free fatty acid of above 1 percent, extra alkali catalyst is introduced to neutralize the effect of soap forming (Javed *et al.,* 2011). This indicates that the oil can be converted to biodiesel using a single stage transesterification.

3.3 Acid value

The acid value is the quantity of carboxylic acid groups present per gram of the raw material. The efficacy of transesterification which can lead to low yield is has a result of high acidic value (Canackci and Gerpen, 2001). Also the acid value is the measurement of corrosive present in free fatty acids and oxidation of products. This implies that the acid value determines the quality of the oil (Ibeto *et al.,* 2012). Acid values (mgKOH/g) of the extracted oils are presented in Table 1. The acidic value of 1.022 mgKOH/g was obtained for maradol while 0.988 and 0.984 mgKOH/g for solo and js22 cultivars respectively. These values were closer to 0.8 mgKOH/g required by ASTM standard as presented in Table 2. The outcome on Table 1 depicts that all the oil specimens has low acid value. This implies that the oil can be transesterified contiguously when the acid value is 2% or less comparing these values with Table 1.2, the values obtained (Table 1) were higher than those ofsafflower and avocado oil (0.8% and 0.805% respectively) which meets with ASTM standards but were far lower than those of groundnut and melon oil (5.99% and 4.76% respectively). The results depicts that the three papaya cultivar seeds are apt for biodiesel production.

3.4 Peroxide value

Peroxide is used to determine the shelf life of the oil. Peroxide values of the three papaya cultivar seed oil were in the range of 5.174 - 5.374 meq/kg w. Although, these values are falls in the acceptable range (4.36 – 9.82) of peroxide value for non – edible oils, but are significantly higher than jatropha oil seed (1.93 meq/kg) and groundnut oil (1.50 meq/kg) (Table 2). This depicts that the oil can easily go rancid, that is the shelf life of the oil can be shorten Oils withhigh percentages of peroxide are unsteady and can stale easily (Nzikou, 2007). This implies that for purposes of biodiesel production, oil extracted should be used immediately after extraction as peroxide values is an index of rancidity and indicates the level of opposition of the oil to peroxidation when store.

3.5 Saponification value

Saponification values is used in checking adulteration of the oil. Saponification value of the oils obtained is 189.95mgKOH/g, 190.17 mgKOH/g and 190.25 mgKOH/g for solo, maradol, and js.22 respectively. The values obtained for all the cultivars are greater than 100 and when compared with ASTM standard (Table 2) indicates that values falls within the range of jatropha oil (188 - 198) and that of cornoil (190.6 mgKOH/g), although the values were lower than those of melon (197.6 mgKOH/g) and avocado oil (246.7mgKOH/g) which had been employed as raw materials for producing biodiesel. This implies that the oil has high saponification values which can leads to soap formation and difficult in separating the product if use for biodiesel production.

3.6 Iodine value

Iodine value defines the content of ricinoleic acid. A higher iodine value indicates higher unsaturated fatty acid content in the oil. Higher unsaturated fatty acids influence better cold flow characteristics but have deleterious effect on oil stability (Akintayo and Bayer. 2012). Iodine value obtained from the seeds were 70.736 (solo), 70.946 (maradol) and 71.502 (js.22) indicating the absence of high levels of unsaturated fatty acids, very common in polyunsaturated drying oils. The iodine values of oil obtained from the three cultivars are in close range obtained from *Luffia cylidrica* (66.37) and *Arachis hypogaea* oil (89.46) as reported by Ibeto *et al.* (2012). The low amount of iodine value gotten shows that the oils of the three cultivars are nondrying oil since their values are below 110 as reported by Ibeto *et al*. (2012) in the classification of oil for biodiesel production. This implies that the oils will be a good feedstock for biodiesel.

Also, when compared to the standard range in Table 2, the iodine values falls within the standard range of 120gI/100g, therefore indicating that the oil is suitable as biodiesel feedstock.

3.7 Refractive index

Refractive index is an important parameter to evaluate the state of a biodiesel since change in biodiesel temperature brings about a cloudy state appears and changes in the index of the refractive (Sadrolhosseini, 2011). Refractive index of the extracted oil are 1.4578 (solo), 1.45812 (maradol) and 1.45788 (js.22). The values obtained are in close range of refractive index obtained from *Arachis hypogea* oil (1.46) (Ibeto *et al.,* 2012). Comparing these values with ASTM standard (Table 2) and other seed oil used in biodiesel production, it was observed that these values were closed with that obtained for groundnut oil (1.447) but lower than that of safflower (1.475), soybeans (1.473) and melon oil. This shows that the oil is suitable as biodiesel feedstock. Also, the general values of refractive index for different oils usually vary from 1.447 and 1.482 (Shahidi, 2005).

3.8 Specific gravity and Density

Specific gravity is a significant criterion for injection systems of a diesel fuel. The values must be sustained in acceptable threshold to allow best air to fuel ratios for complete ignition. Dense biodiesel or its blend can produce partial ignition and dust matter release (Galadima, 2008).

Specific gravity the oils were 0.904, 0.903 and 0.903 for solo, maradol and js.22 respectively. When compared in Table 2, they were found to be amidst the established range of 0.87-0.0.90 for biodiesel (Agunbiade and Adewole, 2014) but were lower than those of melon (0.919), jatropha (0.9186) and avocado oil (0.923).This makes it fitting oil for biodiesel fusion trial.

3.9 Cloud point and Pour point

Cooling of fuel occurs at a temperature when there is visibility of wax and the temperature at which this occurs is the cloud point (Agunbiade and Adewole, 2014). Solo and js.22 has higher cloud point when compared with maradol as shown in Table1. This shows that the oil extracted from maradol does not form wax quickly and thus would not clog filters and pipes of engine easily. Table 1 shows that maradol has the lowest pour point (-7.76) when compared to the other two varieties (- 0.78 and - 2.88 for solo and js 22 respectively) having indicating that its oil is suitable for use in cold regions having temperature below 0°C.The cloud point and pour point obtained indicates that the oil is appropriate for use in cold regions

Table 1: The Properties of the extracted oil

Sample	PP (°c)	CP (°c)	SG	A_cV (mgKOH/g)	I_cV (gI/100g)	P_cV (meq/Kg)	F_fF_fA (%)	RI	Oil Yield (%)	SV (mgKOH/g)	Density (g/cm^3)
Solo	-0.78	1.26	0.904	0.988	70.736	5.294	0.4962	1.4578	22.522	189.95	0.7
Maradol	-7.76	-0.78	0.903	1.022	70.946	5.144	0.5142	1.4581	27.988	190.17	0.74
JS.22	-2.88	1.14	0.903	0.994	71.502	5.318	0.4996	1.4578	22.588	190.25	0.69

PP: Pour point; CP: Cloud point; SG: Specific gravity; A_cV: Acid value; I_cV: Iodine value

F_fF_fA: Free fatty acid; RI: Refractive index; P_cV: Peroxide value; SV: Saponification value

Table 2: Comparison of the Extracted Oils with Other Seed Oils and Standard

Oil Properties Tested	Experimental pawpaw seed oil			Some other common seed oil								
	Solo	Maradol	Js.22	Groundnut	Safflower	Soya beans	Corn Oil	Melon	Cotton seed	Avocado	Jatropha	Standard
Oil yield (%)	22.522	27.988	22.588	47.2	30.5	21.0	4.5	NN	22.9	NN	46	30% min
Acid value (mgKOH/g)	0.988	1.022	0.994	5.99	0.8	1.0	3.0	4.76	1.4	0.805	1.0-38.2	0.8
Free fatty Acid (%)	0.4962	0.5142	0.4996	3.01	0.4	0.5	1.5	2.38	0.7	0.37	4.22	≤1
Saponification Value (mgKOH/g)	189.95	190.17	190.25	193.2	191.0	193.0	190.6	197.6	195.0	246.7	188-198	190-194
Peroxide Value (mEq/kg)	5.294	5.144	5.318	1.50	NA	NA	NA	NA	NA	NA	1.93	NA
Refractive Index	1.4578	1.45812	1.45788	1.449	1.475	1.473	1.467	1.478	1.470	1.462	NA	NA
Density (g/cm^3)	0.823	0.782	0.73	NA	NA	NA	NA	NA	NA	NA	NA	NA
Specific Gravity	0.904	0.903	0.903	NN	NN	NN	NN	0.919	0.915	0.923	0.9186	0.87-0.90
Pour Point (°C)	-0.78	-7.76	-2.88	NA	NA	NA	NA	NA	NA	NA	8	NA
Cloud Point (°C)	1.26	-0.78	1.14	NA	NA	NA	NA	NA	NA	NA	NA	NA

Source (ASTM, 2011) Note: NA = Not available

IV. CONCLUSION AND RECOMMENDATIONS

4.1 Conclusion

Investigation into biodiesel properties of oil extracted from three cultivars of pawpaw seeds (solo, maradol and js 22) was carried out. Chemical method was used in carrying out oil extraction from the three cultivars. The extracted oil was characterized to find out some physiochemical constituents of the oil as being suitable for biodiesel production. The properties of the oil investigated are oil yield, acid value, free fatty acid value, pour point, cloud point, density, Refractive index, saponification value, specific gravity. These properties were further compared with other seed oil and ASTM standards for biodiesel production. The results indicated that the oil can be exploited for biodiesel production. It was further observed that maradol variety has the most suitable properties that can be exploited in cold temperate regions due to the value of its cloud point and pour point.

4.2 Recommendations

It is recommended that further investigation should be carried out other properties such as flash point, calorific value and cetane number that could not be carried out due to paucity of fund. The oil is as well recommended for trial as biodiesel production through transesterification process.

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