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Papaya Seed Oil as Potential Source for Bio-Fuel Production

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Abstract

The Carica papaya seed oil (CPSO) was extracted by solvent process. The physicochemical characteristics of the oil were studied. The seed has an oil yield of 31.60% which is commercially sustainable. The CPSO was analysed for specific gravity (0.94), viscosity at 40 ^{0}C (49.20 cp), iodine value (53.80 g/100g), and saponification value (158.60 mg/g), peroxide value (6.70 m mol/kg), calorific value (44.37 MJ/kg) and free fatty acid (0.34) using standard methods. Fatty acid profile of the oil indicted it is highly unsaturated (67.4%), this implies that the unsaturated fatty acid of the seed oil is more than the saturated one. The implication of this is that the oil will not solidify easily when applied in engines but will flow as oil and not fat. Thus, it can be concluded that the seed can be utilized for the extraction of oil which can be used as feedstock for bio-fuel production.

Key words: *Carica papaya seed, solvent extraction, fatty acid, physicochemical properties.*

Introduction

Papaya (*Carica papaya* L.), belonging to the family Caricaceae, exists in almost all tropical and subtropical regions of the world. According to Food and Agriculture Organization (FAO, 2007), it is an invaluable plant that is prevalent throughout tropical Africa and Nigeria is the third largest producer globally (Oseni*et al*, 2018). Being a tree-like herbaceous plant, papaya bears fruits throughout the year. Different forms, sizes, colour of the flesh of papaya are existed depending on the variety. The flesh of the papaya fruit may vary from yellow to orange or reddish. Each fruit may have a large number of seeds which are usually attached in rows to the interior of the fruit (Noorzianna*et al*., 2014). The papaya seed is presently a waste product as it is often discarded after eaten the papaya fruits owing to its very inadequate uses at the moment. There are rare information's on this quite underutilized seed despite its importance (Kamini and Milap, 2017). Beside, Makanjuola and Makanjuola, 2018), reported that by-products of papaya i.e. seeds and skin which are often disposed off producing environmental and ecological problems related to creation of insects, rodents as well as economic problem contained essential nutrients that are valuable to human and animals for life sustenance. There has been a considerable interest with regard to the oil potential of papaya seeds.

There has been growing interest in the use of vegetable oils as lubricants and hydraulic fluids due to the reduction of the world's crude oil reserve combine with the consumption rate, increase in petroleum prices and scarcities, issues related to management, harmfulness and environmental issues arising from conventional petroleum-based fluids have brought about renewed attention in the use of bio-based resources. Emphasis on the development of renewable, biodegradable, and environmentally friendly industrial fluids, such as diesel, lubricants and other fuels have raised the need to search for alternative renewable fuels (Bilal et al., 2013 and Louis and Toyib, 2017). The need for an alternative to fossil fuels has stimulated extensive research in recent years. Fossil fuels are nonrenewable sources of energy which generate pollutants and are associated to global warming, climate change and even some incurable diseases. Beside, high emissions of CO_2, NOx, SO_2, particulate matter, poly aromatic hydrocarbons and hydro-carbons are created during the using of fossil fuel and producing environmental problems. These facts have converged in the search for renewable energy sources, such as biofuels and bioethanol. Biodiesel has been recognised as one of the remarkable options for at least complementing conventional fuels. However, it's produced from renewable biological sources such as vegetable oils and fats have been reviewed widely. Its advantages over petroleum based diesel cannot be overemphasized: it is safe, renewable, non-toxic, and biodegradable; it contains no sulphur; and it is a better lubricant. In addition, its use stimulates numerous societal benefits: rural revitalization, creation of new jobs, and reduced global warming (Aransiola*et al*.,2014 and Kamini and Milap 2017) . Besides, the feedstock alone represents about 75%

of the overall biodiesel production cost. Therefore, minimizing the cost of biodiesel production has been the main agenda for biodiesel producers in order to be competitive with petroleum-derived diesel, it is crucial to employ inexpensive feedstock to replace expensive refined oils (Yadessa and Jorge, 2017).

Vegetable oil or the fatty acids which are used in producing biolubricant are also cheaper than petroleum based lubricant. Beside, biolubricant have a better emollient property than petroleum based lubricant, it also has a higher viscosity index and flash point. A high viscosity index is a necessary to make sure the lubricant maintains its thickness even at high temperatures. However, the high flash point indicates low risk of fire at high temperature. Even though biolubricant seem to be a better choice of lubricant, it still has some disadvantages. The presence of a double bond in the fatty acids causes the poor oxidative stability which is important for a longer projection life of the lubricant. These fatty acids contain bis-allylic hydrogen that provides a space for free radical attack and this can be improved by some chemical modification such as epoxidation and oxirane ring opening. Other than that, the vegetable oils also have poor thermal stability. This is due to the β- hydrogen of hydroxyl group that presence on the glycerol, the backbone in triacylglycerol. This can also be overcome by substituting the glycerol with polyols that does not contain β-hydrogen atoms (Vanitah et al., 2015). Besides, the utilization of oil in various applications is largely determined by the yield, composition, physical and chemical properties of the oil. However, different physical and chemical parameters of vegetable oil were used to monitor the compositional quality of oils. These physicochemical parameters include iodine value (IV), saponification value (SV), viscosity, density and peroxide value (PV). Several researchers studied the impact of temperature on the stability, viscosity, peroxide value, and iodine value to assess the quality and functionality of the oil (Aladekoyi*et al*., 2016 and Erum*et al*., 2014).

The seeds contain 30%–34% oil with nutritional and functional properties similar to that of olive oil and can be utilised as the feedstock for biodiesel synthesis (Mohammad *et al.,* 2019). However, Soxhet extraction of papaya seed oil using *n*-hexane to achieved yield of 34.3% was reported by Wong and Othman (2015).

Oil Extraction System

Oil extraction is the first stage in bio-fuel production. There are many methods of oil extraction from the original sources such as seeds, fruits, and other oil bearing materials. A simple mechanical press can be used for extracting the oil without further processing. This process is also known as cold pressing. Not all seeds are suitable for extraction using mechanical press; some of them involve a complex process such as a combination of pressing, cooking and solvent extraction. However, solvent extraction is the process in which the oil is removed from a solid by means of a liquid solvent, the chemical extraction using n-hexane method results in the highest oil yield, relatively simple and quick and solvent can be recovered and reused, reducing cost significantly which makes it the most commonly used method (Mohammed *et al.*, 2019 and Yadessa and Jorge, 2017).

Chemical Extraction

Removing one constituent from a solid by means of a liquid solvent is known as chemical extraction. It is also known as solvent extraction process. The rate of extraction of oil depends on the type of liquid chosen, particle sizes, temperature and agitation of the solvent. The most common solvent used in the chemical extraction process is hexane due to its low cost and low toxicity. However, most researchers have found the chemical extraction process as convenient to extract oil from both papaya seed and stone fruit seed (Mohammed *et al.*, 2019). A standard weight of crushed Jatropha seed was placed in a 5 L three neck flask. Hexane was used as solvent to extract oil. The volume of hexane needed was determined by the ratio of 6:1. A reflux condenser was fitted and the mixture was heated at 60°C and stirred for about 8 h, the resulting oil and solvent mixture were filtered to remove the suspended solids. Then, the mixture was placed in a rotary evaporator to evaporate the solvent and thus, Jatroph a oil was obtained (Bilal *et al.*,2013). Conversely, plant seeds were detached manually from papaya and rambutan fruit, the seeds were dried in an oven at 60 ºC for 24 hours. The dried seeds were pulverized into small particles and the oil were extracted using n-hexane for 8 hours in a Soxhlet apparatus. The extracted oil was then undergone evaporation using a rotary evaporator to remove the remaining solvent (Wong and Othman, 2015). Oil was extracted from the dried seeds (with residual moisture of around 7%). Besides, the extraction was achieved in a Soxhlet apparatus with n-hexane organic solvent at a temperature of 68 °C for a period of 6 hours. The solvent was recovered at 45 °C in a rotary vacuum evaporator, and the oil was dried in a water bath at 90 °C for one hour (Maria and Damião, 2016). Soxhlet extraction, which is traditionally considered as the extraction method resulting with the maximum yield, was carried out in a classic Soxhlet extractor in the presence of ethanol, diethyl ether, petroleum ether, hexane or acetone as a solvent. 10 g of safflower seed mixed with 200 mL solvents was processed until the oil in ground seeds were all played out. After the operation completed, the solvent was removed until the oil came to the constant weighing (Takadas and Doker, 2017).

This paper presents an analysis of the physical–chemical properties of the crude oil. The properties evaluated are acid number, iodine value, specific gravity, peroxide value, saponification value, viscosity and calorific value also investigated to verify if those are real potential sources for high-quality oil for biofuel production.

MATERIALS AND METHODS

Materials

Most of the chemicals used in this investigation were of analytical grade. They were obtained from Department of Chemical Engineering and Agricultural and Bio-recourses Engineering, Federal University of Technology Minna, Niger State. The equipment were obtained from Department of Chemical Engineering and Agricultural and Bio-recourses Engineering, Federal University of Technology Minna

Methods

Fresh Pawpaw seeds were harvested randomly from different locations in Bida, Bida Local Government Area in Niger state to have a good representation of the samples.

Preparation of the sample

The matured seeds from ripe Pawpaw seed were removed freshly and the seeds separated manually. The seeds were washed with water at least 3 times to remove the gelatinous and 3 to 5 days of sun drying were required to completely dry 1 kg of fresh feed. The seeds were milled mechanically by small milling machine in the market, and stored in a clean bottle for extraction process (Aladekoyi*et al.*, 2016 and Elvianto and Erni 2017)

Extraction Procedure

A pre oven dried thimble was weighed with analytical weighing balance (w_1). 10g of the powdered sample was added to it (w_2), and put inside the soxhlet apparatus. 500ml boiling flask was filled to 2/3 with solvent (Hexane) and fitted to the soxhlet carrying the condenser to cool the solvent. It was heated gently and allowed to siphon after soaking the sample for 6 hours. After the extraction, the thimble with the extracted sample were removed and allow to dry at low temperature in an oven for few minutes, cool and weighed (w_3). % crude oil was determined from each stage. The process was done until the required quantity of the oil has been collected. The oil was stored at room temperature until it is required for analysis (Aladekoyi, Karimu and Jide, 2016).

Chemical properties

The determination of peroxide, iodine and saponification values, unsaponifiable matter and free fatty acid (FFA) contents was carried out using the methods of Palm Oil Research Institute of Malaysia. (PORIM 1995).

Saponification value:

Accurately weigh out 2 g of oil into a 250ml of conical flask, add 25ml of alcoholic KOH and dissolve the oil completely. Connect air condenser to the flask and boil for about 30 min on a boiling water bath. Cool to room temperature; add 2 drops of phenolphthalein indicator and mix. Titrate against standard 0.5 N Hcl until the pink colour disappears. Treat blank similarly in absence of oil.

$$\text{Saponification value} = \frac{(Blank + Titre) \times 100}{Weight\ of\ oil}$$

Iodine value: Weight out 0.2g of oil into 500 ml conical flask. Add 20 mlof chloroform and dissolve the oil completely. Keep in dark for30 min. Add 20 ml of KI solution and mix well. Titrate against0.1 N $Na_2S_2O_3$ solution using starch as an indicator withvigorous shaking to extract iodine from the chloroform layer.Conduct blank similarly in absence of oil.−

Iodine number $= \frac{A \times N \times 0.1269 \times 100}{Weight\ of\ oil}$

Where, A= ml of $Na_2S_2O_3$

N=Normality of $Na_2S_2O_3$

Free fatty acid content: The free fatty acid in oil was estimated by titrating it againstKOH in presence of phenolphthalein indicator. The acid numberis defined in 1 g of sample. However, the free fatty acid isexpressed as oleic equivalents. 1 ml N/10 KOH= 0.028g Oleicacid

Specific gravity determination

An empty 5 ml specific gravity bottle was weighed out and the weight was recorded. It was filled with water and reweighed. The water was poured off, and the bottle weighed again.

Viscosity determination: The viscosity of the oil was determined using a universal torsion viscometer. The oil was inserted into a vessel on the sample table so that the cylinder was centrally immersed from 0-360. The fly wheel was rotated from rest. The viscosity in centipoises, at a given speed cylinder combination was obtained by multiplying the instrument readings with appropriate multiplying factor given on the calibration chart.

Peroxide value

1.0 g of the oil was weighed into dry test tube, followed by addition of 1.0 g of powered potassium iodide and 20 ml of a solvent mixture of glacial acetic acid and chloroform (2:1). This was placed in a boiling water bath so that the contents are boiled for 30 seconds. The contents were quickly poured into a flask containing 20 ml of 5 % potassium iodide. The tube was washed twice with 25 ml of distilled water and poured into the flask. It was titrated with 0.002 M sodium thiosulphate using starch indicator. The blank titration was done also.

RESULTS AND DISCUSSION

Physicochemical characteristics and oxidative stability of seed oil

The results of the physicochemical characterization and the oxidative stability of the oil extracted from papaya seeds are presented in Table 1. The papaya seed oil had a low iodine value (53.8 g/100 g) which confirmed it as non-drying oil. Other oils classified as non-drying are macadamia, olive, and peanut oils. Low iodine values for Carica papaya L. seed oil (79.95 g/100 g) was also obtained by (Cassia et al., 2010). The saponification value (158 mg KOH/.g of oil) in close agreement with (155 mg KOH/.g of oil) reported by Syed et al., (2011) which are lower when compare with the value of 190.00 (mg of KOH/g of oil) reported by Eriola*et al.*.(2012) when study Statistical Approach to the Optimization of Oil from Beniseed (*Sesamumindicum*) Oilseeds, suggesting lower concentration of triglycerides with lows saponification . However, the Acid value is a measure of the free fatty acids in oil. The higher the acid value found, the higher the level of free fatty acids which translates into decreased oil quality. The free fatty acids and the peroxide values are valuable measures of oil quality. The papaya seed oil showed 1.08% of free fatty acids and 6.70 m mol.kg–1 of peroxide value. These values are not considered high since crude vegetable oil maximum contents of 5% of free fatty acids and 10 m mol.kg–1 of peroxide value may be verified (Cassia *et al*., 2010). Fatty acids compositions of the extracted Papaya seed oil are presented in Table 2 below which show high level of oleic acid. Beside, oleic acid concentration, being an indication of its high oxidation stability

Table1. Physicochemical characteristics of pawpaw seed oil

S/NO	Parameters	Determined value
1	Iodine value (g I/100g)	53.80
2	Peroxide value (M mol/kg)	6.70
3	Calorific value (Mj/kg)	44.37
4	Specific gravity	0.94
5	FFA (%)	1.08
6	Viscosity at 40 ^{0}C	49.20
7	Saponification value (mg KOH/g)	158.60
8	Oil yield (%)	31.60

Table2. Fatty acids compositions of the extracted Papaya seed oil

Acid	Composition	%
Benzene, (isothiocyanatomethyl)	C_{6-4}	1.4
2,4-Di-tert-butylphenol	C_{8-3}	1.2
Dodecanoic acid	C_{9-0}	1.7
Tetradecanoic acid	C_{11-4}	1.5
1-Octadecene	C_{11-5}	0.9
Neophytadiene	C_{12-1}	0.7
Pentadecanoic acid	C_{12-6}	0.6
Hexadecanoic acid, methyl ester	C_{13-1}	0.3
Palmitoleic acid	$C_{13.6}$	1.1
Palmitoleic acid	C_{13-7}	1.0
n-Hexadecanoic acid	C_{14-0}	29.6
2,2-Bis[4'-cyanooxyphenyl]propane	C_{14-4}	0.8
Heptadecanoic acid	C_{14-7}	0.4
9,12-Octadecadienoic acid (Z,Z)-, methyl ester	C_{15-4}	0.2
9-Octadecenoic acid, methyl ester, (E)-	C_{15-5}	0.5
Oleic Acid	C_{16-6}	42.0
Octadecanoic acid	C_{16-8}	5.5
9,12-Octadecadienoic acid (Z,Z)-	C_{17-0}	1.3
9,12-Octadecadienoic acid (Z,Z)-	C_{17-6}	0.3
Octadec-9-enoic acid	C_{19-6}	0.4
Cyclotetracosane	C_{19-8}	0.4
Oleic Acid	C_{20-4}	0.2
cis-Vaccenic acid	C_{22-1}0.2	
17- Pentatriacontene	C_{22-7}0.3	
9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester	C_{24-5}	0.8
Squalene	C_{26-1}	0.5
3-[3-(3,4-Dimethoxy-phenyl)-acryloyl]-6-methyl-pyran-2,4-dione	C_{27-8}	1.2
5-Cholestene-3-ol, 24-methyl-	C_{33-6}	1.9
Stigmasterol	C_{34-3}	0.9

SAFA = 32.6

MUFA = 1.7

PUFA = 65.7

SAFA—Saturated fatty acid; MUFAs—Monounsaturated fatty acids, PUFAs—Polyunsaturated fatty acids.

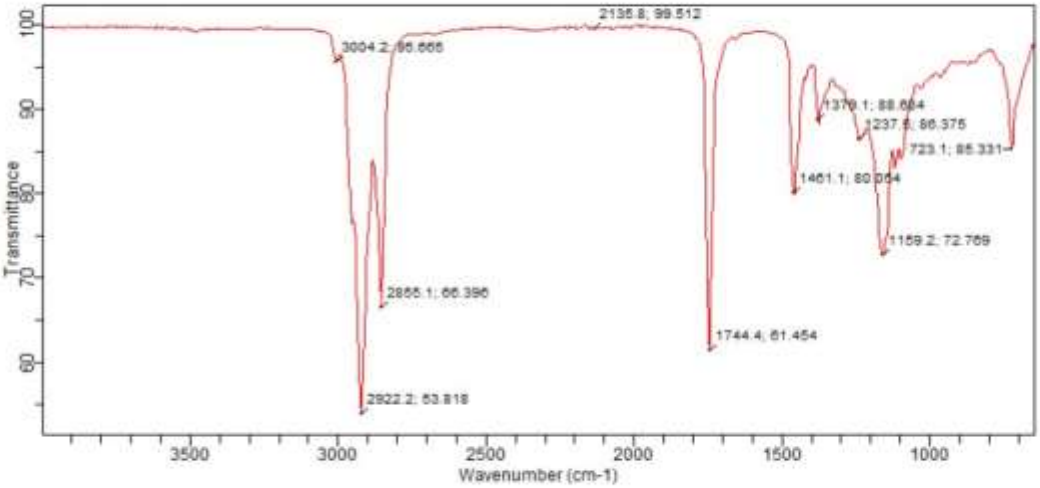

Figure 4. Fourier transforms infrared (FTIR) spectrum of Papaya seed oil (PSO)

The most important functional groups, wave number, band assignment and absorption intensity of absorption peaks detected in the FTIR spectrum of the PSO are presented in Table 6. The peak at 1744.4 cm^{-1} corresponds to the bending vibration of $–CH_3$ present in the PSO sample, which is shown in Figure 4. The peak in the region of 2900–3000 cm^{-1} represents the CH_2 asymmetric stretching vibration. The peak of stretching of the carbonyl group (–C=O) is 2855 cm^{-1} located in the region of 2900–2800 cm^{-1} which is common for esters. The fingerprint region of 1500– 900 cm^{-1} is the major spectrum from the PSO ester which has a peak at 1461.1 cm^{-1}, corresponding to the stretching vibration.

Table 3. Functional Groups of Papaya Seed Oil Detected in the FTIR Spectrum

Frequency cm^{-1}	Group Attribution	Vibration Type	Functional Group	Absorption Intensity
3004.2	-C-H	Asymmetric stretching Vibration	Alkyl	Strong
2922.2	$-CH_2$	Asymmetric stretching Vibration	Aromatic	Strong
2855.1	-C=O	Stretching Carbonyl Vibration	Carbonyl	Strong
2135.8	$-CH_2$	Shear-type Vibration	Alkanes	Weak

1744.4	$-CH_3$	Bending Vibration	Alkanes	Weak
1461.1	C-O-C	Anti-symmetric stretching Vibration	Esters	Middling
1379.1	C-O-C	Anti-symmetric stretching Vibration	Esters	Middling
1237.5	C-O-C	Anti-symmetric stretching Vibration	Esters	Weak
1159.2	C-O-C	Anti-symmetric stretching Vibration	Ether	Weak
723.1	$-CH_2$	Plane rocking Vibration	Aromatic	Weak

Conclusions

The study of papaya seeds oil showed high oil content (31.6 %), the seed has sufficient oil content and the oil has suitable properties which are similar with other oils that have been applied for bio-fuel production. However, the physicochemical properties of papaya seed oil are in close agreement with that of Syed *et al*, (2011).The high percentage of unsaturated fatty acids would make the oil an acceptable substitute for other highly unsaturated oils. Information provided by present study is of great importance and revealed industrial utilization of the papaya seeds oil as feedstock for bio-fusel production

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