

Investigation of Solvents Efficiencies on Oil Extraction and Biodiesel Production from Hura Crepitans Seeds

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Abstract: Solvent extraction of oil from seeds of *Hura crepitans* was carried out with a Soxhlet apparatus, using various solvents. Based on the percentage oil (w/w) obtained from the pulverized seed cotyledon, n-hexane was found to be the most efficient solvent for oil extraction. Base-catalyzed trans-esterification, using methanol, was done to process biodiesel from the extracted oil with 95% (v/v) biodiesel yield. The biodiesel was subsequently tested for its fuel properties and found to conform well to ASTM and EN biodiesel standards.

Keywords: Hura crepitans, solvent extraction, base-catalyzed, biodiesel

1. Introduction

Many seed-bearing plants in Nigeria in particular and Africa in general are yet to be fully exploited to derive all the potential benefits they possess. This is due to insufficient research based information on their chemical and industrial significance. One of such seed-bearing plants is Hura crepitans, commonly referred to as Sandbox tree.

Hura crepitans (Sandbox tree) is a tropical plant belonging to the family of Euphorbiaceae (spurge family). It is commonly planted in the cities and villages of the south-western part of Nigeria. In Nigeria, it is known as "Odan Mecca" by the Kabba people of Kogi State, Nigeria and as "Aroyin" by the Ijesha people of Osun State, Nigeria,[1]. The trees are about 9 meters tall on the average, with the masculine and feminine flowers on the same tree. The flowers of the masculine are of dark red colour arranged laterally on the small branches. The bark of the tree is covered with lots of short spines when it grows; the woody fruits resemble small pumpkin pods in which the seeds are housed with about 13 seeds in a pod [2]. The unripe seed pods are green in colour, but when ripe, they turn brown. On maturation and drying, the pods explode violently to liberate their seeds to the surrounding. The seeds are small and brown in colour, with an average diameter of about 1-5cm.

2. Literature Survey

2.1. Oil Extraction

There are several common methods of oil extraction from oil-bearing seeds. These include the following: Mechanical Method, Rendering Method and Solvent Extraction Method. Among the three mentioned, solvent extraction method has proved to be the most efficient method of extraction, hence the decision to use solvent extraction for the current study on extraction efficiency. Solvent extraction is so efficient that,

using suitable solvents, oil can still be extracted from cakes (which may still contain up to 15 percent fat) that were obtained from mechanical pressing and rendering methods [3]

2.2. Biodiesel Production

Biodiesel is amber to yellow liquid containing a mixture of monoalkyl esters of long chain fatty acids. It is produced by reacting together an alcohol and a vegetable oil or fat in the presence of sodium or potassium hydroxide as catalyst. The reaction is called transesterification and yields glycerol as a co-product [4].

Three basic methods are used for biodiesel production from fats and oils:

1. Base-catalysed transesterification of the fat or oil
2. Direct acid-catalysed transesterification of the fat or oil
3. Conversion of the fat or oil to its fatty acids and then to biodiesel.

Almost all biodiesel is produced using base-catalysed transesterification because it is the most economical process requiring low temperatures, and pressures and producing over 98% conversion yield.

2.2.1. Mixing of Alcohol and Catalyst

The catalyst is typically sodium hydroxide (caustic soda) or potassium hydroxide (potash). It is dissolved in the alcohol using a standard agitator or mixer. The alcohol/catalyst mix is then charged into a closed reaction vessel and the oil or fat is added. The system from here on is totally closed to the atmosphere to prevent the loss of alcohol. The reaction mix

is kept just above the boiling point of the alcohol (around 160°F) to speed up the reaction and the reaction takes place. Recommended reaction time varies from 1 to 8 hours, and some systems recommend the reaction take place at room temperature. Excess alcohol is normally used to ensure total conversion of the fat or oil to its esters. Care must be taken to monitor the amount of water and free fatty acids in the incoming oil or fat. If the free fatty acid level or water level is too high it may cause problems with soap formation and the separation of the glycerin by-product downstream [5].

2.2.2. Separation

Once the reaction is complete, two major products exist: glycerin and biodiesel. Each has a substantial amount of the excess methanol that was used in the reaction. The reacted mixture is sometimes neutralized at this step if needed. The glycerin phase is much denser than the biodiesel phase and the two can be gravity separated with glycerin simply drawn off the bottom of the settling vessel. In some cases, a centrifuge is used to separate the two materials faster [4].

2.2.3. Alcohol Removal

Once the glycerin and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation. In other systems, the alcohol is removed and the mixture neutralized before the glycerin and esters have been separated. In either case, the alcohol is recovered using distillation equipment and is re-used. Care must be taken to ensure no water accumulates in the recovered alcohol stream.

2.2.4. Glycerin Neutralization

The glycerin by-product contains unused catalyst and soaps that are neutralized with an acid and sent to storage as crude glycerin. In some cases the salt formed during this phase is recovered for use as fertilizer. In most cases the salt is left in the glycerin. Water and alcohol are removed to produce 80 – 88 % pure glycerin that is ready to be sold as crude glycerin. In more sophisticated operations, the glycerin is distilled to 99% or higher purity and sold into the cosmetic and pharmaceutical markets.

2.2.5. Methyl Ester Wash

Once separated from the glycerin, the biodiesel is sometimes purified by washing gently with warm water to remove residual catalyst or soaps, dried, and sent to storage. In some processes this step is unnecessary. This is normally the end of the production process resulting in a clear amber-yellow liquid with a viscosity similar to petrodiesel. In some systems the biodiesel is distilled in an additional step to remove small amounts of color bodies to produce a colorless biodiesel.

2.3. Biodiesel Quality

Prior to use as a commercial fuel, the finished biodiesel must be analyzed using sophisticated analytical equipment to ensure it meets any required specifications. The most important aspects of biodiesel production to ensure trouble free operation in diesel engines are:

- Complete Reaction
- Removal of Glycerin
- Removal of Catalyst
- Removal of Alcohol
- Absence of Free Fatty Acids

As mentioned earlier, biodiesel is clear, amber to yellow liquid with a viscosity similar to petrodiesel. It is rapidly biodegradable and non-toxic. It has a flash point of 160°C and is thus classified as a non-flammable liquid. Biodiesel can be mixed with petrodiesel in any proportion and can be used as an additive in formulations of diesel to increase the lubricity of pure ultra-low sulphur petrodiesel fuel. Biodiesel has excellent solvent properties, better than petrodiesel, and has been known to break down deposits of residue in the fuel lines of vehicles that have previously been run on petrol. Biodiesel products have a problem of gelling when the temperatures get below 4.4°C or so, depending on the mix of esters. Biodiesel is also hydrophilic. The common international standard for biodiesel is EN 14214 [5].

3. Previous Work

Solvent extraction with the Soxhlet apparatus was first described by Frantz Ron Soxhlet in 1879. In this method, the sample is dried, ground into small particles and placed in a porous cellulose thimble. The thimble is placed in an extractor chamber, which is suspended above a flask containing the solvent and below a condenser. The flask is heated and the solvent evaporates and moves up into the condenser where it is converted into a liquid that trickles into the extraction chamber containing the sample. The extraction chamber is designed so that when the solvent surrounding the sample exceeds a certain level it overflows and trickles back down into the boiling flask. The solvent is then redistilled from the solution in the flask and condensed in the extraction chamber. The mass of the remaining lipid (oil) is then measured and hence the percentage of oil in the initial sample is then calculated.

In 2002, Professor Isiaka Amoo, while working with his research team on Hura crepitans seeds, found out that the crude fat content of the seeds was as high as 53.81% [6]. This finding serves as a great motivation to find out, among common solvents, which has the highest efficiency to extract oil from this seed and the possibility of utilizing such oil for the production of biodiesel.

A variety of biolipids (fats/ oils) can be used to produce biodiesel. They include virgin vegetable oil feedstock (e.g rapeseed, sunflower seeds, mustard seed, palm and soya bean oils,) waste vegetable oil and animal fats (e.g. lard and tallow); even algae are a promising oil source for biodiesel production. Biodiesel is a novel, renewable, alternative transportation fuel which has combustion properties very similar to those of petroleum diesel. It operates in combustion-ignition diesel engines with little or no engine modification and is a possible candidate to replace fossil fuels as the world's primary transportation energy source [4].

Biodiesel can be used alone (i.e. neat) or blended with conventional petrodiesel. When used as a pure fuel, it is known as B100. Its blend with petrodiesel is designated "BXX where XX = represents the percentage of biodiesel in

the blend. For example, fuel containing 20% biodiesel is labeled B20 [5].

4. Methods / Approach

4.1. Investigation of Solvents Efficiencies Using Different Solvents in the Quantitative Extraction of Oil from Hura crepitans Seeds

The solvent extraction method was used to extract oil from dried, pulverized Hura crepitans seed cotyledons. 2 grams of the sample was weighed into a filter paper folded and tied neatly. This was placed in the thimble of the Soxhlet apparatus. Oil extraction was done exhaustively under reflux for 16hrs with petroleum ether as the solvent into the round bottom flask which was previously oven-dried and weighed. The flask was disconnected at the end of the extraction, heated gently at 40°C to allow evaporation of the solvent from the oil, cooled and weighed. The weight of oil extracted was obtained by difference and expressed as a percentage. The procedure was repeated with other solvents: n-hexane, benzene, diethylether, chloroform, acetone, and ethanol. The results obtained for these various solvents are as presented in Table 1;

Table 1: Percentage Oil Yield by Different Solvents

Solvent	Crude Fat (%)
Chloroform	54.32
n-hexane	58.87
Ethanol	4.80
Propanone	54.90
Diethylether	53.81
Petroleum ether	52.80
Benzene	51.97

4.2. Production of Biodiesel from Hura crepitans Seed Oil

300ml of Hura crepitans seed oil (HCSO) was measured into a beaker and placed on a hot plate set at low heat. This was done to remove traces of water, reduce oil viscosity to make for easy stirring and help the conversion to biodiesel go faster. 1.05g of sodium hydroxide pellet was weighed into another beaker and 60cm³ of methanol which corresponds to 20% of oil used was added. The mixture was stirred continuously until all the sodium hydroxide pellets dissolved. The methanol-sodium hydroxide mixture was poured into a 2-litre capacity reaction vessel, the warm HCSO was added, vessel closed tightly and maintained at 60°C for 1 hour. This mixture was stirred at intervals of 5 to 7 minutes while still in the reaction vessel. In the biodiesel production process, the methanol reacts with the oil to give two products – glycerol and biodiesel. The mixture of the products was poured into a separating funnel; the glycerol settled to the bottom of the funnel and was drained off. After that, the biodiesel was distilled to remove excess methanol, purified by washing gently with warm water to remove residual catalyst or soaps and dried with anhydrous calcium tetraoxosulphate (VI). The product was then transferred into a sample bottle and labeled as; “HCSO Biodiesel”.

4.3. Characterization of “HCSO Biodiesel”

The fuel properties of “HCSO Biodiesel” were determined and used to characterize it. These properties are; specific gravity, cloud point, flash point, pour point, kinematic viscosity, total acid number and calorific value. These determinations that were made are compared with ASTM D6751 [7] and EN 14214 [8] Standards for Biodiesel as shown in Table 2;

Table 2: Comparison of Fuel Properties of HCSO Biodiesel with Standards Provided by ASTM and EN

Fuel Properties	“HCSO Biodiesel”	ASTM D6751	EN 14214
Flash point (°C)	153	>130	> 101
Pour point (°C)	-3.0	-15 to 13	-15 to 13
Cloud point (°C)	6.0		
Specific gravity	0.8918	0.87 to 0.98	0.86 to 0.90
Viscosity (mm ² /s)	7.32	1.90 to 6.0	3.50 to 5.00
Acid value (mgKOH/g)	0.14	0.80 (max)	0.50 (max)
Calorific value(J/g)	10629.30		
Biodiesel yield (% v/v)	95		

4.3.1. Determination of Flash Point

ASTM method D 93 [9] of the American Society of Testing Materials (ASTM) was employed in this determination. 70cm³ the biodiesel was measured into the partially closed test cup of a Pensky-Martens (closed cap tester) Flashpoint apparatus, provided with a stirrer and thermometer the cup was heated gradually with continuous stirring. At regular intervals of 3 minutes, a small flame was directed into the cup with simultaneous interruption of stirring. The temperature, at which the sample flashed, on application of the test flame, was observed and recorded as the flash point.

4.3.2. Determination of Pour Point

The standard test method for determination of Pour Point of petroleum oils, ASTM D 97 [10], was adopted. The biodiesel sample was poured into the test jar to the level marked. The jar was closed tightly with a cork carrying the pour point thermometer. The thermometer was adjusted so that its bulb and the beginning of the capillary was immersed 3mm below the surface of the oil. A ring gasket was placed around the test jar and then lowered into the cooling bath. The biodiesel was cooled at a specific rate and examined for flow at 3°C interval. The lowest temperature at which the oil ceased to flow was observed and recorded as the pour point.

4.3.3. Determination of Kinematic Viscosity

The standard test method for kinematic viscosity of transparent and opaque liquids, ASTM D 445[11], was used for the determination. 30cm³ of the biodiesel sample was measured into the viscometer tube. The tube was placed in the viscometer bath containing a silicone oil heating medium. The rubber pump was used to draw up the biodiesel into the upper bulb of the viscometer and the time, t, required for it to flow under gravity to the lower bulb was determined with a stop-watch. The procedure was repeated to obtain triplicate readings. The average of the readings was

noted and recorded. The kinetic viscosity was calculated using the formula;

$$V = c t$$

where,

V = kinematic viscosity (in centistokes, cSt)

c = calibration constant of the viscometer (cSt/s)

t = average flow time of biodiesel

4.3.4. Determination of Specific Gravity (S.G)

The specific gravity bottle method was used for this determination. The bottle was weighed empty and when filled with distilled water, to obtain the weight of water by difference. The water was then poured out and the bottle was wiped dry, filled with biodiesel and weighed again to obtain the weight of biodiesel. The specific gravity of the biodiesel was calculated as follows:

$$S. G. = \frac{\text{Mass of a given volume of biodiesel}}{\text{mass of equal volume of water}}$$

4.3.5. Determination of Cloud Point

10cm³ of the biodiesel was measured and transferred into a test tube. The beaker was filled with crushed ice and a hole large enough to accommodate the test tube was made. The test tube and the content were placed in the hole in the ice. A thermometer was inserted into the biodiesel. The temperature at which the biodiesel began to appear cloudy was noted. The test tube was removed and warmed with the hand to clarify the biodiesel. The process was repeated and the average temperature at which the biodiesel began to turn cloudy was calculated and recorded as the cloud point.

4.3.6. Determination of Calorific Value

A wick lamp was used to perform this experiment. Some biodiesel was placed in the lamp and weighed (w_1). A small beaker containing 10ml (10g) of water and a thermometer was clamped directly above the lamp. The lamp was ignited, using the biodiesel as fuel, to heat the water. The water was stirred with the thermometer and when its temperature had risen to 27°C, the flame of the lamp was put out immediately and allowed to cool. The lamp with its content was then weighed again (w_2). The calorific value of the biodiesel in J/g was calculated as follows:

$$\text{Calorific value (J/g)} = \frac{(4.2m\theta)}{(w_1 - w_2)}$$

where,

m = mass of water,

S = specific heat capacity of water = 4.2

θ = temperature rise

w_1 and w_2 are the weights of lamp and content before and after ignition respectively.

4.3.7. Determination of Total Acid Number

10g of the biodiesel sample was weighed into a 250ml conical flask. 100ml of the titration solvent and 0.5ml of the indicator were added. The flask was swirled until the biodiesel dissolved. The mixture (now yellow orange in colour) was immediately titrated with the 0.1M alcoholic KOH solution until the colour changed to green or green brown at the end point. A blank titration was carried out on 100ml of the titration solvent without adding the biodiesel. The total acid number was calculated as follows:

$$\text{Total Acid Number (mgKOH/g)} = \frac{(A - B) \times 56.1 \times N}{W}$$

where,

A = titre value of sample

B = titre value of blank

N = normality of KOH

W = weight of sample

4. Results and Discussion

The efficiencies of different solvents on oil extraction from Hura crepitans seed were compared on the basis of the percentage by weight of oil extracted and the results are presented in Table 1. The results show that n-hexane, which extracted 59% crude fat, is the best solvent while ethanol, extracting only 5% crude fat, is the worst solvent for extracting oil from Hura crepitans seed. Generally, the solvent efficiency decreases in this order: n-hexane > propanone > chloroform > diethyl ether > petroleum ether > benzene > ethanol, that is, non-polar to polar.

Results of laboratory tests conducted to determine the fuel properties of "HCSO Biodiesel" which was derived from Hura crepitans seed and its comparison with ASTM D6751 and EN 14214 specifications for biodiesel are presented in Table 2. ASTM D 6751 and EN 14214 are international standards that describe the minimum requirements for a mixture of alkyl esters to be considered biodiesel. Most of the properties for "HCSO Biodiesel" conform well to the standards specifications, except for its very high pour point (-3°C) and viscosity (7.32 mm²/s). This shows that significant engine modification involving a fuel system pre-heater is required to ensure free flow of this fuel before "HCSO Biodiesel" can be safely used for diesel engines in very cold climate. The high flash point shows that HCSO biodiesel is a non-flammable liquid compared to petroleum diesel which has a flash point of 64°C and will be safer in the event of a crash. Its low acid value, 0.14 mg KOH/g, of the biodiesel means that problems associated with fuel acidity such as corrosion and formation of deposits within the engine will not be encountered when it is used as fuel.

5. Conclusion

This work has shown that among common organic solvents such as; propanone, chloroform, diethyl ether, petroleum ether, benzene and ethanol, n-hexane is the most efficient solvent to extract oil from seeds of Hura crepitans. Besides,

biodiesel obtained from a base-catalyzed trans-esterification of oil from *Hura crepitans* possess remarkable fuel qualities for use in diesel engines, especially in tropical climate.

6. Future scope

Further research work should focus on testing other types of catalysts for the trans-esterification reaction and development of continuous process, instead of batch process, for the production of biodiesel. More work should be done to investigate of the effects of reaction time, reactor speed and oil pretreatment on overall biodiesel yield, quality and stability during storage.

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