Production of Biodiesel from (fruit seeds) Custard Apple Seed (Annona Squamosa)

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***Abstract*: Rising prices and depletion of fossil fuels make it very necessary today to find an alternative fuel made from non-edible oil seeds (biodiesel). This paper describes the transesterification of Custard apple seed oil using methanol in the presence of potassium hydroxide catalyst at temperatures below 65 °C. The viscosity of biodiesel made from Custard apple seed oil is close to that of commercial diesel. Custard apple seed oil is characterized by GC (Gas Chromatography) analysis, showing density, flash point, cloud point, pour point, dynamics Key biodiesel properties such as viscosity, ash, and carbon residue are determined and compared to those from ASTM based Biodiesel standards and commercial diesel. This study will facilitate biodiesel production from custard apple seed oil (Annona squamosa) and increase the value of custard apple fruit.**

***Keywords*: biodiesel, custard apple seed oil, production, transesterification.**

1. Introduction

Despite rationalization measures being implemented, energy consumption is steadily increasing around the world [1]. Liquid fossil fuels are the most important and most commonly used fuels for mobile work machines. Given that the entire development of mobile work machines is based on the use of liquid fossil fuels, a deviation from this trend towards mass development and the use of new engine designs suitable for another fuel is unlikely. Research focused on finding fuels that could be adapted to existing engine designs and met standards for renewability, ecology and operational safety. Meeting the above criteria is the basis for successfully replacing fossil fuels with other types of fuels. Over the past decade, biodiesel has become the most widely used renewable liquid fuel due to its ability to meet the specific requirements of the aforementioned standards. This means that no engine modifications or fuel injection system modifications are required to use biodiesel. The exceptions are older engine designs that require replacement of sealant and fuel injection hoses [2].

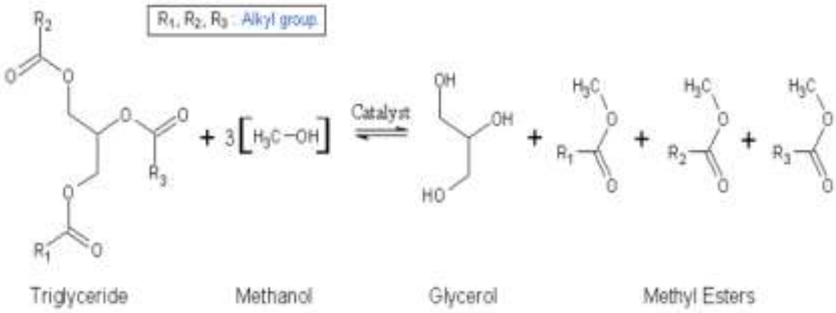
The Custard apple, shown in Figure 1, belongs to the family Annuaceae, whose scientific name is the genus Annuola, is common in deciduous forests and is wildly cultivated in various parts of India. It is native to the West Indies. It is now grown in India and other tropical countries. The literature of many research papers proves the medicinal properties of all parts of the annuus [3-6]. Also known as Sweetsop and Sugar Apple (English), Seetaaphala and Amritaphala (Kannada), Atoa and Shariffa (Hindi) [7]. Biophysicallimits:-Altitude 0-2000m, average annual temperature up to 41°C, average annual rainfall more than 700mm, Soil type Anunreiji tolerates a wide range of soils and thrives in fertile, well-drained, deep rocky soils, but prefers loose sandy loam. [8]. It has been reported that 26.8% is contained in the seeds of Annuoli, as shown in Figure 2 [9]. Agricultural residues and by-products or waste from food processing are often viewed as a problem. After treatment, a large amount of plant material is often left unapplied. Converting such materials into valuable resources can go a long way in reducing waste. In this sense, residue recycling is of great interest from an economic point of view [10]. The transesterification reaction formally requires an alcohol to oil molar ratio of 3.A molar ratio of 1, but actually 6:1 should be applied for the reaction to proceed properly in high yield. The transesterification reaction usually takes about 1 hour at normal pressure and reaction temperature of 60-65 °C (for methanol) [11].

Figure 1. Collection of Custard Apples

Figure 2. Collection of Custard Apple seeds.

1.1 Biodiesel transesterification:

The transesterification process consists of a series of three consecutive reversible reactions. H. Conversion of triglycerides to diglycerides followed by conversion of diglycerides to monoglycerides. Glycerides were converted to glycerol and ester molecules at each step. The methanolysis transesterification reaction is represented by the following equation: [12].



If the oil contains more than 4% free fatty acids (FFA), a two-step transesterification is applied to convert the high FFA oils to their monoesters [13]. The first step, acid-catalyzed esterification, reduces the free fatty acid content of the oil. The second step, an alkaline transesterification process, converts the product of the first step into its monoester and glycerol [14].

2. Experimental method:

2.1. Oil extraction:

Extraction of oil from custard apple seeds was performed using a mechanical press and solvent extraction by a Soxhlet apparatus using methanol as solvent. Yields are shown in Table 1.

Table-1: comparison of oil extraction [between mechanical and chemical]

Quantity	Type of Extraction	
	Mechanical expeller	Soxhelt extraction
1 kg of seeds	180-200 ml of oil	250-260 ml of oil

2.1.1. Soxhlet extraction (laboratory scale):

To check the oil content of custard apple seeds

Procedure:

1.50 grams of fully ripe Custard apple seeds were ground and included in the test setup.
2. Add 150 ml of methanol to the round-bottomed flask as solvent.
3. The reaction was held at 65°C for the number of cycles.
4. Methanol obtained by retaining oil in a round bottom flask.
5. Pour the oil in the piston into the measuring cup and measure it.
6. The amount of oil obtained is estimated at approximately 1 kg of seeds.

Results obtained during testing:

For 50 grams of seeds, 30 cycles yield 13 ml of oil. (For custard apple seed, 1 cycle time = 5 minutes 36 seconds). 1000 grams of seeds = 260 ml of oil. The percentage of oil obtained is 26%.

2.1.2. Mechanical expeller (production scale):

Procedure:

1. Seeds are pulverized with a mechanical press to obtain oil. (Mechanical expeller capacity is 30 kg/h, 3 passes).
2. Grind 5kg seeds per batch, pass each batch of seeds 5 times to grind full oil.
3. The resulting oil was filtered and collected in a glass reagent vessel.

4. Let the filtered oil sit for 10-12 hours to allow fine dust particles to settle.
5. After filtration and sedimentation, store the oil in a test tube bottle.

2.2. Determination of free fatty acid (FFA) content in crude oil:

2.2.1: Preparation of 0.1 normal (0.1N) NaOH solution:

Weigh 4 grams of NaOH and transfer to an Erlenmeyer flask containing 1 liter of water. A solution in which NaOH is completely dissolved by constant stirring is called a 0.1N NaOH solution. (NaOH has a molecular weight of 40, so a 0.1N solution contains 4g per liter).

2.2.2: Titration and calculation of free fatty acid content in crude oil:

Take 25 ml of 0.1N NaOH solution in a burette, take 10 g of Custard apple seed oil in an Erlenmeyer flask, add 50 ml of isopropyl alcohol, add 5 to 6 drops of phenolphthalein as an indicator, and shake well. This is titrated against a 0.1N NaOH solution until it turns pink. This is the endpoint indicator and the formula can be used to find FFA levels in oil.

2.2.3: FFA calculation:

FFA Content = $28.2 \times Normality\ of\ NaOH \times Titration\ value\ /\ weight\ of\ the\ oil$

FFA Content = 28.2×0.1×6.3 10.5gm = 1.692

Note that the above formula contains 28.2 which is the molecular weight of oleic acid divided by ten. Oils are not made of only oleic acid hence this formula results in small errors, normally accepted.

2.3. Transesterification:

Procedure:

Take 1 liter of custard apple seed oil in a three-necked flask equipped with a reflux condenser, heat the oil to 60 ° C, add 300 ml of methanol and 10 g of potassium hydroxide catalyst. Process for about 90 minutes, as shown in Figure 3. Run Pour the oil into the separatory funnel and let it sit for about 7-8 hours, forming two layers as shown in Figure 4 below. The top layer is biodiesel and the bottom layer is glycerin. Separate glycerin and biodiesel. The yield from this process has been found to be 88-90% biodiesel. (850-900ml).

Figure-3: Transesterification setup

Figure-4: Separation of two layers

2.4. Determination of physicochemical properties:

2.4.1. Viscosity:

Kinematic viscosity is the resistance offered by a layer of liquid on top of another layer. Viscosity is important in determining optimal handling, storage, and operating conditions. The fuel must have suitable flow characteristics to achieve sufficient fuel delivery to the injectors at various operating temperatures. High viscosity can cause fuel flow problems and stall.

Procedure:

Fill the flask of the Kanonen Fenske viscometer [tube #100, direct form] with biodiesel. Insert the viscometer tube into the viscometer water bath device. Heat the oil to 40°C and keep it at that temperature for 20-30 minutes. After 30 min, open the tube, aspirate the oil, and simultaneously start the stopwatch when the oil reaches the starting point mark. Stop the stopwatch when the oil flow reaches the bottom mark on the piston. Note the seconds on the stopwatch. Kinematic Viscosity (Centistokes) (Cst) = (Seconds x Standard Factor for Piston Viscometer used for testing) [Note:The standard viscometer coefficient provided by the manufacturer is 0.0238]

2.4.2 Density:

A hydrometer is an instrument used to measure the specific gravity (specific gravity) of biodiesel. This is the ratio of water densities. A hydrometer is made of glass and consists of a cylindrical shaft and a ball weighed by a mercury or lead bullet that is held upright. A hydrometer includes a paper scale on the shaft so that the specific gravity can be read directly.

Procedure:

Weigh 500ml of biodiesel into a clean, dry graduated cylinder. Calm down on biodiesel. Carefully lower the hydrometer into the biodiesel in the cylinder and allow it to float freely. Note that the biodiesel surface contacts the hydrometer stem. The reading will be the specific gravity multiplied by a thousand to give the density.

2.4.3. Flash point:

The lowest temperature at which the vapor of a flammable liquid ignites briefly in air is called the flash point and correlates with the ignitability of the fuel. A low flash point may indicate residual methanol left over from the conversion process. Flash point is often used as a descriptive property of liquid fuels and is also used to characterize the fire hazard of liquids. "Flash point" refers to both flammable and combustible liquids.

Procedure:

Add the measured biodiesel to the mark displayed on the flashpoint gauge. Heat the oil and stir the oil periodically. Outside fire is periodically introduced near an opening provided in the device until lightning is observed. Record the temperature when a flash is observed. The temperature during flame treatment is the flash point of biodiesel.

3. Results and discussion

The percentage composition of free fatty acids present in custard apple seed oil was obtained by gas chromatography analysis and is shown in Table 2.

Table-2: The fatty acid composition of custard apple seed oil by gas chromatography

Sl.NO	Parameters	Results
1	Oleic Acid	39.72%
2	Linoleic Acid	29.17%
3	palmitic Acid	17.79%
4	Stearic Acid	4.29%
5	Behenic Acid	2.01%
6	Linolenic Acid	1.37%
7	Arachidionic Acid	1.06%
8	Lauric Acid	0.08%
9	Caproic Acid	Nil
10	Caprillic Acid	Nil
11	Capric Acid	Nil
12	Myristic Acid	Nil
13	Erucic Acid	Nil
14	Lignoceric Acid	Nil

The gas chromatography results table shows that oleic acid (39.72%) is the major component. I understand. The physico-chemical properties listed below of the produced biodiesel were determined and compared to ASTM biodiesel standards and commercial diesel, and the results are shown in Table 3.

Table-3: The physicochemical properties of custard apple biodiesel comparisons with the ASTM biodiesel standard and commercially available diesel

Sl.NO	properties	Units	Experimental Values			
			Biodiesel (Custard apple)	Biodiesel Standard values(ASTM)	Commercially Available Diesel	Protocall
1	Kinematic viscocity@40^0 c	centistokes	5.712	1.9-6.0	2.54	ASTM D445
2	Flash point	^{0}c	150	130	54	ASTM D93
3	Density	Kg/m^3	865	870-900	820	ASTM D4052
4	Cloud point	^{0}c	2	-3 to 12	-28 to -7	ASTM D2500
5	Ash content	%w/w	Nil	-------	0.02max	ASTM D482
6	Pour point	^{0}c	5	-15 to 10	5.6 to 11.1	ASTM D97
7	Carbon Residue	%w/w	Nil	-------	0.05max	ASTM D524
8	Calorific value	KJ/Kg K	37510.7	37000 to 42500	43500	ASTM D240

3.1. Viscosity:
Among the common parameters of biodiesel, viscosity controls the properties of diesel injection. The viscosity values of Custard Apple Biodiesel are within the ASTM Biodiesel specifications.
3.2. Density:
The higher density of custard apple biodiesel compared to commercial diesel is due to its higher molecular weight and the presence of triglyceride molecules. The density of Custard apple biodiesel is within the ASTM biodiesel specification.
3.3. Flash point:
The flash point of Pudding Apple Biodiesel is closer to the ASTM Biodiesel standard.
3.4. Calorific value:
Calorific value is the energy released in the form of heat when a hydrocarbon (fuel) burns completely with oxygen under standard conditions. Chemical reactions typically involve hydrocarbons reacting with oxygen to form carbon dioxide, water, and heat. The resulting calorific value is within ASTM biodiesel specifications.

Conclusion
By observing all the consequences of biodiesel from Custard apple seed oil, Solvent extraction emerged as the best method when the various oil extraction processes were compared. The entire process of extracting oil from custard apple seeds takes three and a half hours, even with the time required for washing. Custard apple seeds can be used as a biodiesel feedstock. All properties are within the range of ASTM biodiesel standards, which may make custard apple kernel a promising factor for using as one of the biodiesel sources.

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