

## PRODUCTION OF BIODIESEL FROM CUSTARD APPLE (*ANNONA SQUAMOSA*) SEEDS

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Received: 15<sup>th</sup> April 2017, Accepted: 23<sup>rd</sup> April 2017, Published: 1<sup>st</sup> May 2017

### Abstract

India is one of the top countries with respect to the increasing population. In accordance to its increasing population there is a simultaneous increase in the demand for the non-renewable resources. In order to maintain the biological balance and satisfy the needs of the increasing population a search for the alternative energy sources is must. One such path is the production of renewable resources. Keeping in view the current need of the population the current work was aimed to produce biodegradable, Biodiesel obtained for the organic waste, the spent seeds of Custard apple. This source can be a very good utility product as there is no special investment required and additionally it can be a source of waste clearance. Here a pure laboratory protocol has been employed to extract the vegetable oil from the seeds of the custard apple. The oil is further treated with the special reagents as per the SOP and the esterification was performed to obtain the diesel along with the useful bio products the soap and glycerine.

### Keywords

### Introduction

#### Biodiesel

Biodiesel is one of the alternative fuels usable in any conventional diesel engine with a little or no modification to the engine or fuel system. Increased utilization of renewable biofuels results in significant micro-economic benefits to both the urban and rural sectors. Also it results in a substantial reduction of unburned hydrocarbons, carbon monoxide and particulate matter. A renewable fuel can be derived from vegetable oils, used oils and animal fats. Biodiesel is not the same thing as raw vegetable oil; rather, it is produced by a chemical process which removes the glycerine and converts the oil into methyl esters. Biodiesel can be used in any concentration with petroleum-based diesel fuel with little or no modification to existing diesel engines. These blended fuels are referred to as "biodiesel blends", and include the percentage of biodiesel in the blend, such as B2 (2%), B5 (5%) or B20 (20%).

Biodiesel is defined as the mono-alkyl esters of fatty acids derived from vegetable oils or animal fats(Knotheet al2006, Coronado et al2008) In

simple terms, biodiesel is the product obtained when a vegetable oil or animal fat is chemically reacted with an alcohol to produce fatty acid alkyl esters. A catalyst such as sodium or potassium hydroxide is required for this reaction and glycerol is produced as a by-product.

#### Natural sources of biodiesel

The biodiesel is produced from nonedible oils, which include Jatropha (*Jatrophacurcas*) oil, Karanja or Honge (*Pongamia* *pinnata/glabra*) seed oil, Polanga (*Calophylluminophyllum*) seed oil, Rubber (*Heveabrasiliensis*) seed oil, Mahua (*Madhucaindica*) oil, Tobacco (*Nicotianatabacum*) seed oil, Bitter almond (*Prunusdulcis*) oil, Castor (*Ricinuscommunis*) seed oil, Okra (*Hibiscusesculentus*) seed oil, Kusum (*Schleicheratrifolia*) oil, Simarouba (*Simaroubaglaucha*), Milo (*Thespesiapulnea*) seed oil, Milk thistle (*Silybummarianum*) seed oil, and wild safflower (*Carthamusoxyacantha Bieb*) seed oil. In the production process of biodiesel. The catalyst concentration, reaction time, and reaction temperature has been studied and optimized. The fuel properties of produced biodiesel have been investigated and compared with the standard specifications for assessing their feasibility to substitute the petroleum fuels

#### Custard apple

*Annonasquamosa* is also called as Sugar apple or Sweetsop. In some regions of world including India the Sugar apple is also called as Custard apple. *Annonasquamosa* is a small, semi-(or late) deciduous, much branched shrub or small tree 3 metres (9.8 fit) to 8 metres (26 fit) tall. The pulp of Custard apple is white tinged yellow, edible and sweetly aromatic. Each carpel contains an oblong, shiny and smooth dark brown to black, 1.3 centimetres (0.51 in) to 1.6 centimetres (0.63 in) long seed. There may be a total of 20 to 38, or perhaps more, seeds in the average fruit (Siddalingappa et al2014). Not only the fruit of custard apple but also its seeds have a lot of benefits. People who enjoy custard apple eat the flesh and peal out the seeds. However sometimes while eating they tend to swallow a seed which could be very harmful; so custard apple are known to be slightly poisonous. These seeds constitute 1/3 of the weight of one custard apple.

In India Custard apple is cultivated in Maharashtra, Andhra Pradesh, Karnataka, Bihar, Orissa and Tamilnadu. According to an estimate made by Indian Council of Agricultural Research (ICAR), custard apple trees are grown in about 40,000hectares and can yield about 4 lakh tones seeds. This in turn can yield 1.12 lakh tonnes oil (Mahalingappa et al. 2014) Custard apple growing regions include Assam, Bihar, Madhya Pradesh, Maharashtra, Odisha, Rajasthan, and Uttar Pradesh, Andhra Pradesh, and Tamil Nadu. According to a 2012 "Times of India" article, approximately 55,000 hectares are dedicated to custard apple cultivation. Pune's Purandar Tehsil district accounts for almost 10 percent of this figure. Along with Maharashtra Gujarat is another large custard apple growing state. The fruit's growing popularity will likely increase production figures substantially in the coming years.

### **Materials and Methods**

#### **Collection of the Seeds:**

The custard apple seeds were collected from field of Madhuban Nursery, At- Gormale Tal - Barshi and local field of Sawargaon region.

#### **Sample Preparation:**

After collection, the seeds were sun dried for a week to remove moisture content. A total of 2 kilograms of dried Custard apple seeds were obtained and ground in mortar and pestle.

#### **Extraction of oil:**

##### **Soxhlet extraction:**

A Soxhlet apparatus consisting of a Soxhlet extraction tube, reflux condenser, 500ml round-bottomed flask, and heating mantel was used to extract the oil from Custard apple seed sample.

##### **Procedure:**

20 grams of fully ripened custard apple seeds were taken and crushed in a mortar and pestle. Filter paper bag were made and the crushed coated seeds were filled in it. Then these bags were placed in the 'extractor' unit of Soxhlet apparatus. 300ml of hexane was taken in the round bottom flask as solvent. Condenser, extractor and the flask were then arranged in a vertical position on a heating mental. The reaction was maintained at 65°C for number of cycles. The condenser was filled in with water and continuous water supply was maintained throughout the process. The temperature was maintained at 65°C for boiling 3 hours. After 3 hrs. hexane with the extracted oil was taken out from the flask; and the seed sample was allowed to dry and then weighed.

#### **Determination of free fatty acid (FFA) content in raw oil:-**

##### **Titration and calculation of free fatty acid content in raw oil:**

##### **Procedure:**

50 ml of 0.1N NaOH solution was taken in the burette. 10 grams of custard apple seed oil was taken in a conical flask and added 50ml of Isopropyl alcohol was added into the conical flask. Solution was kept on hot water bath for 2-3 minutes to allow complete dissolution of oil in alcohol. When clear solution was appeared, it was taken for titration. Phenolphthalein indicator (5-6 drops) was added. This solution was titrated against 0.1N NaOH solution until colours turns from yellow colour to permanent pink colour.

#### **FFA calculation:**

##### **Formula:**

$$FFA = \frac{28.2 \times \text{Normality of NaOH} \times (\text{CBR of sample} - \text{CBR of blank})}{\text{Weight of oil}}$$

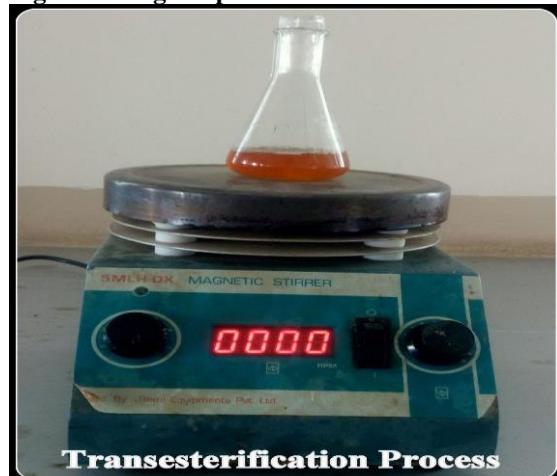
Where, 28.2 = The above formula contains 28.2 which is the molecular weight of oleic acid divided by ten. Oils are not made of only oleic acid hence this formula results in small errors, normally accepted.

#### **Biodiesel production through Trans Esterification:**

##### **Procedure**

50ml of custard apple seed oil was taken in a conical flask, and heated up to 60°C. 30ml of methanol and 0.5gms of potassium hydroxide was added as catalyst. The process was run for 90minutes. Then the oil was transferred into separating funnel and allowed for separation.(7-8 hrs.). Then two layers were formed in which upper layer is biodiesel and lower layer is glycerine. The glycerine and biodiesel was separated from each other. Then the crude biodiesel was obtained.

**Fig 1 showing the process of Trans Esterification**



#### **Purification of biodiesel**

- I. Water wash treatment
- II. Vaporization of water

### **Physicochemical properties of biodiesel:**

#### **Emulsification test:**

The emulsification test is carried out to check the purity of biodiesel. The equal volume of biodiesel and water mixed with each other and shaken vigorously. Checked the phases after 10 minutes were clear or not. If the lower phase is clear, the biodiesel is said to be pure and if not, the impurities are present.

#### **pH of biodiesel**

When an acid is poured into water, it gives up hydrogen (H) to the water. When a base is poured into water, it gives up hydroxide (OH) to the water. Firstly the pH of crude biodiesel was checked and then again checked after washing of biodiesel with distilled water. The pH was measured by digital pH meter.

#### **Specific gravity**

##### **Specific gravity of biodiesel:-**

The specific gravity of biodiesel varies with its fatty acid composition and its glycerine content both free and bound. A denser biodiesel has higher energy content and will give better mileage and increased power. Since the fatty acids content dictates the specific gravity, a denser vegetable oil will process into a denser biodiesel.

#### **Formula**

$$\text{Specific gravity} = \frac{Z - X}{Y - X}$$

#### **Density**

Density is an important property of petroleum products being part of product specifications. Fuel density is a key property that affects engine performance. Because fuel injection pumps meter fuel by volume, not by mass, a greater or lesser mass of fuel is injected depending upon its density. Thus, the air-fuel ratio and energy content within the combustion chamber are influenced by fuel density. In general, densities of biodiesel fuels are slightly higher than those of petroleum diesel.

Density of biodiesel by dividing its mass (gm.) by the volume (ml) of the liquid.

#### **Formula:**

*Density of biodiesel*

$$= \frac{\text{mass of biodiesel(gm)}}{\text{volume of biodiesel(ml)}}$$

#### **Kinematic viscosity:**

The viscosity is important in determining optimum handling, storage, and operational conditions. Fuel must have suitable flow characteristics to ensure that an adequate supply reaches injectors at different operating temperatures. High viscosity can cause fuel flow problems and lead to stall out.

#### **Formula:-**

Kinematic viscosity (mm<sup>2</sup>/sec) = (Number of seconds × standard factor of the bulb viscometer used for testing)

Where,

The standard viscometer factor as specified by manufacturer is 0.01.

#### **Cloud Point:**

"The cloud point is the temperature at which a cloud of wax crystals first appears in a fuel sample that is cooled". The cloud point was determined by visually inspecting for a haze to become visible as the fuel is cooled (in a refrigerator). As a liquid was cooled, a temperature at which the larger fuel molecules begin to form crystals was reached. With continued cooling, more crystals form and agglomerate until the entire fuel mass begins to solidify. The temperature at which crystals begin to appear is called the 'cloud point'

#### **Pour point:**

A second measure of the low temperature performance of diesel/biodiesel fuels is the pour point. The pour point is the lowest temperature at which fuel samples will not flow. Therefore, the pour point provides an index of the lowest temperature of the fuel's utility for certain applications. The pour point also has implications for the handling of fuels during cold temperatures.

#### **Flash point:**

The lowest temperature at which the vapour of a combustible liquid can be made to ignite momentarily in air is identified as the flash point and correlates to ignitability of fuel. Low flash point can indicate residual methanol remaining from the conversion process. The flash point is often used as a descriptive characteristic of liquid fuel and it is also used to characterize the fire hazards of liquids. "Flash point" refers to both flammable liquids and combustible liquids.

#### **Ash content:**

Ash consists of the residue left when the fuel is heated to a sufficiently high temperature that combustible material burns and leaves as CO<sub>2</sub> and H<sub>2</sub>O.

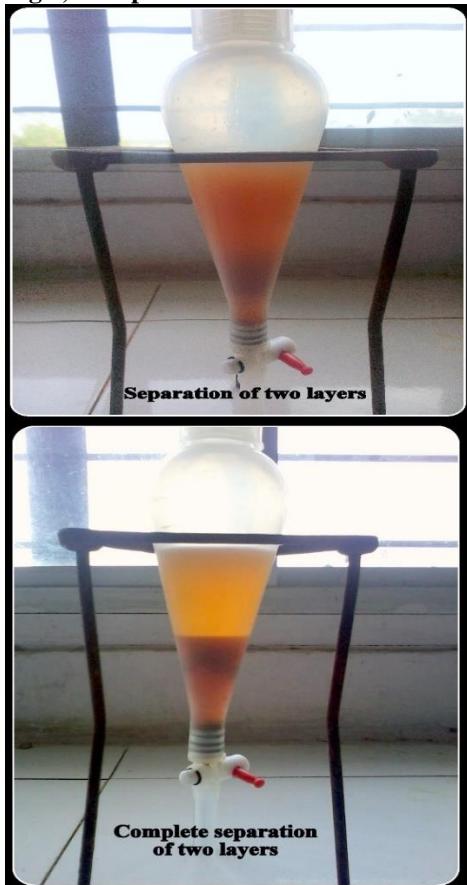
#### **Formula:**

$$\text{Ash content\%} = \frac{\text{weight of the ash}}{\text{weight of the biodiesel}} \times 100$$

#### **Results and Discussion:**

Initially the seeds were ground and the vegetable oil was extracted. Which was used for further treatment. The below figures indicate the several steps in series performed to obtain pure biodiesel.

**Fig 2, 3: Separation of Biodiesel**



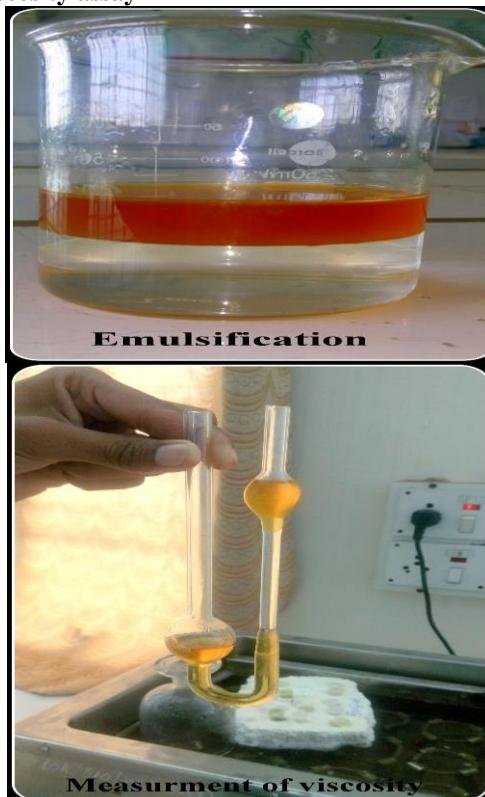
Once the two layers of aqueous and non-aqueous has been separated the crude layer of diesel is processed for purification. The below figures 4, 5 and 6 indicate the purification protocol for the final preparation of pure diesel.

**Fig 4, 5, 6 Purification of biodiesel**



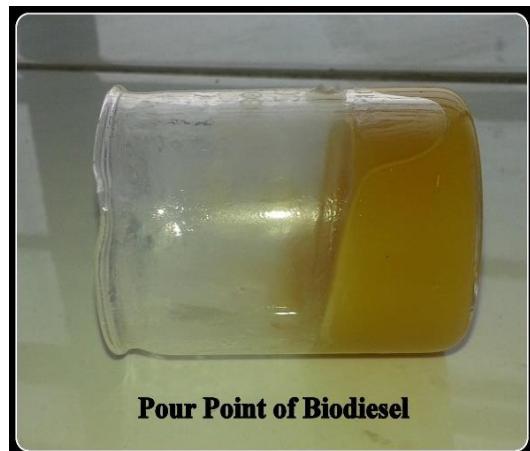
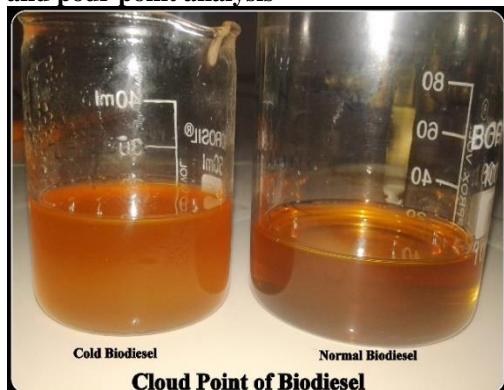
The pure product is then used for emulsification test and conducting viscosity assays. The pictures are shown below:

**Fig 7, 8: Showing the emulsification test and viscosity assay**



This was followed by analysing the Cloud point and pour point of the diesel obtained.

**Fig 9, 10 showing the Cloud point determination and pour point analysis**



**Table no.1. Physicochemical properties of biodiesel comparison with ASTM biodiesel standard and commercial available diesel**

Sr. No.	Physicochemical test	Obtained value of Custard Apple biodiesel	ASTM range of biodiesel	Range of Commercially available diesel	Units
1	Density	0.904	0.870 – 0.900	0.845 to 0.920	g/cm <sup>3</sup>
2	Specific gravity	0.90	0.8 – 0.9	0.8 – 0.9	–
3	Kinematic viscosity (40°C)	4.9	1.9 – 6.0	1.3 to 4.1	mm <sup>2</sup> /s
4	Cloud point	2	-3 to 12	-28 to -7	°C
5	Pour point	-11	-15 to 10	-35 to -15	°C
6	Flash point	160	130 to 170	60 to 80	°C
7	Ash content	0.04%	-	0.02%	%w/w
8	Colour	Golden yellow	Golden yellow	–	–

### Conclusion

The above work involves the production of biodiesel from the seeds of the custard apple. The vegetable oil was extracted from the seeds which were processed for diesel extraction. The crude oil obtained was further purified using various techniques and the final product was analysed. The pure diesel was analysed for its viscosity, Pour point,

Specific Gravity, Flash point, Ash content, and Colour. All the properties were further compared with the standard ASTM values and commercial diesel values. It was found that all these parameters were within the standard range and comparable to the commercial diesel. Thus this procedure can be followed with several other vegetable products to obtain the renewable diesel.

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