Extraction of Straight Oil and Development of Methyl Ester of Sour Garcinia Straight Oil by Transesterification Process

Basavasagar[1], Narasinga[1],Umesh[1], Yeshwanth[1], Sharanappa Godiganur[2]
1. Student, School of Mechanical Engineering REVA University Bangalore
2. Professor School of Mechanical Engineering REVA University Bangalore

Abstract— In search of a suitable fuel alternative to fast depleting fossil fuel and oil reserves and in serious consideration of the environmental issues associated with the extensive use of fuels based on petrochemicals, research work is in progress worldwide,Thesourgarciniatreesarewidelyavailableandgrowintropicalregions ofAsiaand Africa and grow in semi evergreen forests of southern Western Ghats of India. The seeds fallen are collected and oil is extracted at village level with expellers, few million tons of oil will be available for lighting lamps in rural area. Growing Garcinia trees would also help in protecting the environment and benefit the farmers as well. The biodiesel produced by the oil of Garcinia is considered as one of the best substitute for diesel. The FFA test is conducted using titration method. As the raw oil consists of high viscosity and free fatty acid (FFA) the three stage standard transesterification method is used to produce biodiesel. The stage wise transesterification removes impurities, wax, gums, etc and the tri glycerides are converted into methyl esters and glycerine. The neat biodiesel is obtained after the removal of glycerine and water wash. Increase in awareness and growth in research in this area can motivate Garcinia gummigutta as the alternative source of fuel by replacing diesel. In the present study attempt has been made to develop the biodiesel from the oil of Sour Garcinia.

Index Terms:garcinia gummigutta, free fatty acid, transesterification, biodiesel, methyl esters.

1. Introduction--Biodiesel (fatty acid alkyl esters) is an alternative diesel fuel derived from the reaction of vegetable oils or lipids and alcohol with or without the presence of a catalyst. Despite the invention of the vegetable oil fueled engine by Rudolf Diesel dated back in the commercially used biodiesel blends for their vehicles such as US, Japan, Brazil, India, and so on. The petroleum fuel is a blessing of God. It plays a vital role in industrial development, transportation, agriculture sector and to meet many other basic human needs. However, the world energy demand is increasing rapidly due to excessive use of the fuels but because of limited reservoirs, the researchers are looking for alternative fuels. Biodiesel can be one of the best alternatives. It is made from the oils of various types of oilseed crops like sunflower, palm, cottonseed, rapeseed, soybean and peanut, and introduced the first diesel engine intended to run on vegetable oil. In 1900 he ran the engine on peanut oil for several hours successfully. In 1912, he predicted that in future the vegetable oil will be a fuel like diesel oil [1]. However due to abundant supply of petro-diesel, R&D activities on vegetable oil were not seriously pursued Vegetable oils have comparable energy density, cetane number, heat of vaporization, and stoichiometric air/fuel ratio with mineral diesel fuel But high viscosity of vegetable oils causes poor fuel atomization, large droplet size and thus high spray jet penetration causing operational problems related to starting ability, ignition, combustionandperformanceanddurabilityproblemsrelatedto deposit formation, carbonization of injector tip, ring sticking and lubricating oildilution.(2,3,)

1.1 **VegetableOilsasaSourcesofBiodiesel**

Vegetable oils are generally composed of triglycerides whose molecular structures are branched and complex. The large molecularsizesofthecomponenttriglyceridesresultintheoils having higher viscosity compared with that of mineral diesel fuel. Due to the presence of double bonds in the molecular structure of vegetable oils, they can be modified easily as per requirement by treating with alcohols. Methyl or ethyl ester of fatty acid which is known as biodiesel is made from vegetable oils by the method known astransestericationmany researchers earlier produced the biodiesel from various vegetable oils. Oils from rapeseed, soyabean, sunflower, mahua, jatropa, neem, and pongamia oils have been successfully converted into biodiesel by transesterification using methanol or ethanol to study the physic chemical properties, performance and emission characteristics in IC engines using biodiesels. Garcinia gummigutta is one amongst the many species, which can yield oil as a source of energy in the form of bio-fuel. (5)

2. Cultivation of Oil Seed Plant inIndia

Garciniagummigutta (Garcinia Tree) is an evergreen, small or medium-sized dioeciously, understory tree, 5 to 20 m tall, about 70 cm dbh (diameter at breast height) with a rounded crown and horizontal or drooping branches. The bark is dark and smooth. Leaves with opposite etiolate, dark green shining in colour are present. Flowers in clusters of 4 to 20 are usually red, but some trees have yellow ones. Petals normally 4 each about 12 mm wide 11 mm long; anthers attached to a pistil lode with a non-functional stigma. Female flowers occur sing- ly or in clusters of up to 4. The stigmatic surface is normally enlarged, and there is no style. Neither male nor female flow- ers produce nectar. Fruit are green, ovoid berry, 5 cm in di- ameter, yellow or red when ripe, with 6 to 8 grooves. Seed 6 to 8, smooth, large, about 5 cm long and 2 cm wide surrounded by a succulent aril. [9]

Biodiesels are mono alkyl ester of long chain fatty acids of vegetable oil or animal fats either from plant or animal meet- ing the standard of ASTM(American Society for Testing and Materials) D6735.Depending on climate and soil conditions. Different nations are looking for different vegetable oils assubstitute of diesel fuel: soybean oil in USA, rapeseed and sun-flower oils in Europe, palm oil in South East Asia and coconut oil in Philippines.(3). In India, the demand for biodiesel for the year 2014-2015 has been estimated as 13.38 million tonnes considering 20% blends of biodiesel with diesel. The area required for growing the Jatropha plantation alone is about 11.19 Million hectares [4]. The use of edible oil resources like mustard, soya bean, sunflower, palm oil etc. for bio-diesel production put heavy competition with food and above that, the demand of edible oils is being met by importing from other countries. The nonedible oil sources seem to be the only option for cultivation, oil extraction and biodiesel production on industrial scale for engine operation.

2.1 General Morphology of Plant, Fruit and OilSeeds

The general morphology of the oil plant and their seeds, the availability and combustion characteristics like density, viscosity, flash point and fire point, cetane number and calorific value of garcinia oil and its blends with diesel oil under test are presented. The world's rapidly dwindling petroleum supply, their raising cost and the growing danger of environmental pollution from these fuels have led to an intensive search of alternative fuels. The use of Garcinia oil as diesel substitute in compression ignition engine has now gained greater importance because of their large population and phenomenal growth rate. Garcinia oil can easily be substituted for hydro- carbons which are scarce worldwide, and save the countries crores of rupees in foreign exchange. It is therefore necessary to develop some means for improving the fuel economy of compression ignition engines and also to investigate the suitability of Garcinia oil for diesel engine operations. If the diesel engine could be fueled on a cleaner fuel such as honge oil, Garcinia oil, it may well be the most desirable engine of the future. The present researchers considered amongseveral

Fig. 2.1 Photograph of Garcinia TreeFig. 2.2 Garcinia Fruits

Fig.2.3 Ripen FruitsFig.2.4 Garcinia seeds

Garciniagummigutta is the scientific name of commonly knownSourgarciniathatbelongstothefamilyofClusiaceae.ItisalsoknownasUppage, Muruganahuliinsomelocallanguages of India. Garciniagummigutta [9], also known as Camboge or Malabar tamarind, found commonly in the evergreen forests of Western Ghats, from Konkan south to Travancore and in the Shola forests of Nigeria up to an altitude of 6000 ft. It flowers in November-February, and fruits ripen in April- May Fruits are in June-July. The seeds of the fruit have fat, commercially known as Kokam butter. Kokum butter is considered nutritive, demulcent, astringent and emollient. It is suit- able for ointments, suppositories.[7-8].

3. Garcinia OilExtraction

Garcinia oil can be extracted from seed mainly by three methods. They are as follows

- Boilingmethod
- Expellermethod
- Solvent extraction method

3.1. Extraction of Oil by Boiling Conventional Method

The finely dried and crushed seeds are then put in boiling wa- ter,heatedat700Cto80oCandthemixtureisstirredtilltheghee floats on upper layer on hot water whereas the heavierresidual waste at the bottom. The liquid fraction contains oil and water, which are further separated by heating so that wa- ter content evaporates from the oil. And the oil is separated. From this process 5 to 10% of oil can be extracted from one kg of Garcinia seeds

3.2 Extraction of Oil by ExpellerMethod

Sour Garcinia oil is extracted from the Sour Garcinia seeds through a mechanical expeller process. By this process 40% of oil could be extracted from one kg of Sour Garcinia seeds from this process

3.3 Extraction of Oil by Solvent ExtractionMethod

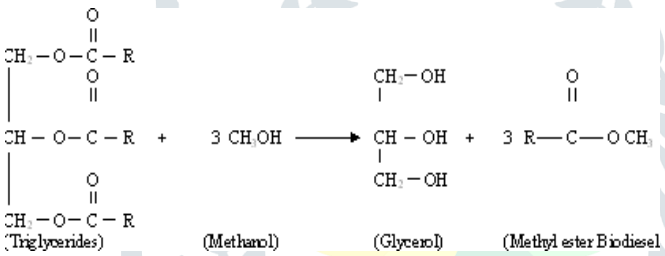
Here the oil is extracted from seeds by using solvent, generally hexane, methanol, etc.From this process 25 to 30% of oil as to be extracted from one kg of Sour Garcinia seeds.

4. Transesterification

Transesterificationis otherwiseknown asalcoholysis. It is the reaction of fat or oil with an alcohol to form esters and glycerin. A catalyst is used to improve the reaction rate and yield [2].In transesterification which is a popular conditioning of vegetable oil of present practice, one ester is converted into another. The reaction is catalyzed by either acid or base involving reaction with an alcohol, typically methanol if a bio-fuel is the desired product. This section deals with steps involved in the preparation of Biodiesel from untreated vegetable oils. A stoichiometric material balance yields the following simplifiedequation.

Fat or oil+3 Methanol → 3 Methyl esters + Glycerol

The chemical reaction involved in thisprocess is shownbelow.



The reaction is catalyzed by either acid or base involving reaction with an alcohol, typically methanol if a bio-fuel is the desired product.

4.1 Determination of free fatty acid in the oil

The standard titration method is used to calculate the FFA present in the oil.NaOH(0.1N) prepared using distilled water and NaOH pellets is taken in a burrette.Calculated quantity of Gacinia oil and isopropyl alcohol is added in a clean and dry 250 ml conical flask.Few drops of NaOH(0.1N) is added and shaken well and the mixture is heated to about 60 oC. Few drops of phenolphthalein indicator is added to this mixture.The titration process is carried out by drop by drop addition of NaOH(0.1N) from the burrette into the mixture in the conical flask, mixing vigorously until a pink faint colour is obtained.The titration is stopped and the burrette reading is noted down to calculate FFA asbelow.

Titration value= 43.5 ml.

FFA=28.2x (Normality of NaOH)x(Titration Value)/weight of oil

FFA= 28.5x0.1x15/10=12%.

4.2 Three Stage: Trans-EsterificationProcess

The experimental setup consists of 3-neck flask with magnetic stirrer and the condenser is fitted to the central neck as shown in the figure 4.1.

4.1 Experimental Trans-esterificationsetup

Fig. 4.2 : Separation of free fatty acid

As the FFA present in the Garcinia oil is 12%,as the Trans- esterification process is carried in 3 stages.

4.2.1Mild acid catalyzedtransesterification

In first stage the raw oil is reacted with methanol in presence of orthophospheric acid in order to neutralize the PH value of sour garcinia oil. The first stage removes organicmatter and other impurities present in the oil in the presence of orthophosphoric acid, used as a reagent. Sour garcinia oil containing the impurities in considerable quantity and causes the transesterification difficulty. Hence, this necessitated the use of first stage. This is a type of reaction that takes place in the presence of methanol and orthophosphoric acid, helps in the separation of impurities which were dissolved in the methanol as an upper layer and oil in the lower layer.

4.2.2 Strong acid catalyzedtransesterification

In second stage the sour garcinia oil is allowed to react with methanol in presence of H_2SO_4 in order to remove free fatty acid from sour garcinia oil.In this stage 1 litre of sour garcinia oil is taken into strong acid and 150ml of methanol and calculated quantity of concentrated H_2SO_4 around 3ml is added to the oil in the flask.And whole set up is kept ready.Then the mixture is kept agitated and heated in the reaction vessel (3-neck flask) at 60oC for 1hr30min.A dark layer was observed at the top layer of the oil.The mixture is then transferred to conical shaped separating funnel and allowed to settle at at least 2 to 3 hours as shown in the figure 4.2. The black acid layer rises up and the bottom acid trans esterified oil is drained back into the 3-neck flask to separate the glycerol.

4.2.3 Base catalyzed transesterification

In third stage transesterification process is done to reduce the complex chain into simpler long chain of ester.In this stage the oil collected in the 3-neck flask from the preveous stage is once again tested for FFA using the same titration method explained earlier and the FFA is calculated to be 3%. On the basis of existing FFA 6.5 gm of NaOH is added to 150 ml of methanol in the separate beaker and mixed to prepare Methoxide mixture and the same is added to the oil present in the 3-neck flask.This mixture of oil and methoxide is agitated and heated at 60°C for 1hr30min.At the end of the process 2 distinct layers are obtained . The mixture is then transferred to conical shaped separating funnel and allowed to settle at least 2 to 3 hours as shown in the figure 5.Glycerine settles at the bottom and the biodiesel is separated at the top. Glycerine is drained out from bottom and the biodiesel is taken for waterwash.

4.3 Water wash

Water washing is done to remove any moisture and emulsion. To do this, water of about 30% by volume of the ester is added and heated the mixture to 120^0C for 1 hour to make the ester free from moisture. After heating, the mixture is once again transferred to the separating funnel where in again the water with any emulsion formed settled at the bottom. The upper layer is pure methyl ester i.e., bio-diesel, ready for the use in diesel engine.The biodiesel obtained is washed 3 times with water to remove the catalyst as shown in the figure 6 to get neat biodiesel which is free frommoisture.

Table 4. 1. The brief description of three stages

Sl. No.	Parameter	1st stage	2nd stage	3rd stage
1	Methanol	150 ml	100 ml	125 ml
2	Orthophospheric acid	3 ml	-	-
3	H2SO4	-	3 ml	-
4	KOH	-	-	6.5 gm
5	Reaction time	1hr30min	1hr30min	1hr30min
6	Settling time	1hr30min	1hr30min	1hr30min
7	Reaction temperature	55°C-60°C	50°C	60°C

Fig.4.3washing with hotwater

Table 4.2: Properties of Sour Garcinia oil & conventional diesel

SI.no	Property	For diesel	Sour Garcinia Oil	Sour Garcinia biodiesel
1	Density in Kg/m3	850	915	880
2	Specific gravity	0.850	0.915	0.880
3	Kinematic viscosity40^{0}Cin CSt	2.83	27.00	4.3
4	Calorific value KJ/Kg	42800	38000	39600
4	Flash pointin ^{0}C	76	163	120
5	Fire point in^{0}C	84	188	150

5. Results andConclusions:

1. The decoction of the fruit rind is administrated to reduce rheumatism and cure improper bowlcomplaints.
2. It is also employed as a rinse for disease of the mouth in cattle. Along with all this the fruit rinds have got many other medicalvalues.
3. Garccinia extract is believed to reduce fat accumulation when consumed.So it is extracted from the dried fruit rind and used in the preparation ofmedicine.
4. Presently due to its global market emerging faster than envisaged, over and unsustainable harvesting of Garcinia have set in theareas.
5. The FFA of raw oil of Garcinia gummigutta commonly known as Sour garcinia is12%.and the standard transesterification process is used to produce biodiesel from it and neat biodiesl isproduced
6. The properties of oil extracted from the seeds of Garcinia gummigutta listed in the Table 4. 2 are similar to the properties of other vegetable oils listed which are widely used to produce biodiesel. Hence Garcinia gummigutta commonly known as Sour garcinia is considered as promising source for biodiesel.
7. Comparison of properties of conventional diesel and Sour Garciniaoil:

References

[1].Williams,A.–Theuseofpalmoilasanalternativediesel fuel‖, Dept. of Fuel and Energy The University of Leeds, Leeds.UK. 123-128.
[2].Schuharardta.(1998),–RicardoSerchelia,Rogerio MatheusVargas, ‖Transesterification of Vegetable oils: A Review.‖, Journal of Brazil Chemistry Society, 9.199- 210.
[3].Meher,L.C.etal(2006),–Technicalaspectsofbiodiesel production by transesterification—a review‖, Journal of Renewable and Sustainable Energy Reviews, 10. 248–268.
[4].B.K.Barnwal,M.P.Sharma.(2005),–Prospectsof biodiesel production from vegetable oils in India‖, Journal of Renewable and Sustainable Energy Reviews, 9.363–378.
[5]. ChristopherW.–Thepracticalimplementationofbio- diesel as an alternative fuel in service motor coaches‖, SAE 973201, 1997.
[6].MontagueX.–Introductionofrapeseedmethylesterin Diesel fuel—the French National Program‖, SAE 962065, 1996.
[7].HohlGH.–Rapeoilmethylesterandusedcookingoil methyl ester as alternative fuels‖, SAE952755,1995.
[8].ZhangY.–Combustionanalysisofestersofsoyabeanoil in a diesel engine‖, SAE 960765, 1996.
[9].GhormadeTK,DeshpandeNV.–Soyabeanoilasan alternative fuels for I. C. engines, Proceedings of Recent Trends in Automotive Fuels‖, Nagpur, India, 2002.
[10].RosaRadu.–Theuseofsunfloweroilindieselengines‖, SAE 972979, 1997.
[11]. Sukumar Puhan, N. Vedaraman, G. Sankaranarayanan andBoppanaV.BharatRam–Performanceandemission study of Mahua oil (madhuca indica oil) ethyl ester in a 4- stroke natural aspirated direct injection diesel engine‖ , Journal of Renewable Energy, Volume 30, Issue 8, pp. 1269- 1278, July2005.
[12]. Shashikant Vilas Ghadge and Hifjur Raheman ― Biodiesel production from mahua (Madhuca indica) oil having high free fatty acids‖ , Journal of Biomass and Bioenergy, Volume 28, Issue 6, pp. 601-605, June 2005.
[13] Rakesh Sarin , Meeta Sharma, S. Sinharay, R.K. Malhotra
–Jatropha–Palmbiodieselblends:AnoptimummixforAsia‖ journal of Fuel vol 86 ,pp1365–1371,2007.
[14]. Rao.G.R & Korwar.G.R ―Research priorities of Pongamia as Biodiesel plant‖, pp. 33-35, Consultative workshop on Scientific strategic for production of non edible oils for use as biofuels, SuTRA(Sustainable Transformation of Rural Area), Indian Institute of Science, Bangalore, India, Sep 6-7, 2003
[15] .N.Robson, -Garcinia Gummigutta Agroforestry4.0,2000.
[16]. Krishnamurthy B, Mathew PA, Rema J, Meenu DIwakaranSoft wood grafting of Garcinia—Indian journal of spices and aromatic crops (2006)-15(1), 63-64.