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Formulation, Investigation & Characterisation of Biodiesel from S. Fimbriata

Mathan Kumar S[1] & Priyanandhini R[2]
[1]*Asst. Professor of Biotechnology, Srinivasan College of Arts & Science, Perambalur-12*
[2]*M.Sc.,Biotechnology (2015-2017), Srinivasan College of Arts & Science, Perambalur-12*
Corresponding Author: Mathan Kumar S

ABSTRACT

DIESEL "THE FOSSIL GOLD"

The world is on the brick of energy crisis due to depletion of fossil fuels. The energy and environmental concern spurred the development of low-cost renewable and sustainable fuel resources. Currently, biodiesel is considered as next generation renewable and sustainable fuel produced from plants or animal lipids. Non-edible resource can provide an alternative source without competing food uses.

In recent years, researchers have tested microwave energy; a non-conventional heating method for extraction and transesterification of lipids from various feed stocks (Shakinaz et al., 2010). The application of microwave irradiation offers a fast, easy route to enhance the reaction rate for synthesis of Fatty acids methyl esters (FAMEs) with reduced time and solvent utilization, using homogenous or heterogeneous catalysis either in batch or continuous system (Hernando et al., 2007). It can be combining to perform single-step extractive transesterification reaction involving appropriate ratio of lipid, solvent and catalyst for biodiesel production (Sharma et al., 2014).

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INTRODUCTION

Brief Description of Biodiesel

Biodiesel is an alternative fuel made from renewable biological sources such as vegetable oils both (edible and non-edible oil) and animal fats According to the US standard specification for biodiesel (American Society for Testing and materials (ASTM) 6751),

Biodiesel has recently attracted much attention all over the world because of its availability, renewability, non toxicity, better gas emissions and its biodegradability. Biodiesel is typically produced by a reaction of a vegetable oil or animal fat with an alcohol such as methanol or ethanol in the presence of a catalyst to yield mono-alkyl esters and glycerin, which is eventually removed. Biodiesel consists of long-chain fatty acid esters (Haas et al., 2001; Abreu et al., 2004) produced by transesterification reaction of vegetable oils with short chain alcohols (Noureddini et al., 1998; Encinar et al., 2002, Harten, 2003). It is compatible with conventional diesel fuel and already used as a commercial fuel in Europe (Knothe et al., 2003; Dorado et al., 2003; Serdari et al., 1999). However, some chemical and physical properties of biodiesel can be affected by oxidation of the fuel during storage (Monyem et al., 2001).

Transesterification

Transesterification is the process of reacting a triglyceride molecule with an excess of alcohol in the presence of a catalyst (KOH, NaOH, NaOCN3, etc.) to produce glycerin and fatty esters. The mixture of fatty esters produced by this reaction is known as biodiesel. The properties of the biodiesel fuel are determined by the amounts of each fatty acid used to produce the esters. Fatty acids are designated by two numbers: the first number denotes the total number of carbon atoms in the fatty acid and the second is the number of double bonds

Production of Biodiesel By Transesterification

Generally, biodiesel is produced by means of transesterification. Transesterification is the reaction of a lipid with an alcohol to form esters and a byproduct, glycerol. It is in principle, the action of one alcohol displacing another from an ester, referred to as alcoholysis (cleavage by an alcohol). In Transesterification mechanism, the carbonyl carbon of the starting ester (RCOOR1) undergoes nucleophilic attack by the incoming alkoxide (R2O−) to give a tetrahedral intermediate, which either reverts to the starting material, or proceeds to the transesterified product (RCOOR2). Transesterification consists of a sequence of three consecutive reversible reactions. The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and finally monoglycerides into glycerol, yielding one ester molecule from each glyceride at each step. The reaction is represented in equation 1. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol. This reaction proceeds well in the presence of some homogeneous catalysts such as potassium hydroxide (KOH)/sodium hydroxide (NaOH). Depending on the undesirable compounds (especially FFA and water), each catalyst has its advantages and disadvantages. Sodium hydroxide is very well accepted and widely used because of its low cost and high product yield. The most common alcohols widely used are methyl alcohol and ethyl alcohol. Among these two, methanol found frequent application in the commercial uses because of its low cost.

$$\text{Triglycerides} + \text{ROH} \rightleftharpoons \text{Diglycerides} + R^1\text{COOR}$$

$$\text{Diglycerides} + \text{ROH} \rightleftharpoons \text{Monoglycerides} + R^2\text{COOR}$$

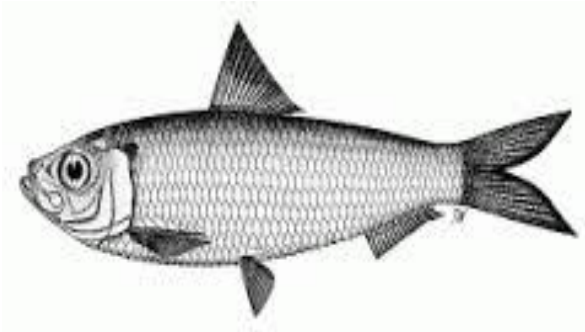
$$\text{Monoglycerides} + \text{ROH} \rightleftharpoons \text{Glycerol} + R^3\text{COOR}$$

Equation 1 Chemistry of transesterification

My Desired Source

India is the 2nd largest producer of fish in the world contributing to 5.43% of global fish production due to longest marine coastline of 8,118 kilometers. The fish market and fish processing industry generates enormous quantities of discarded fish waste approximately 1/3rd part such as head, viscera, tail, skin, liver, eyes, fins etc. which is considered as loss. The marine fish oil extracted from discard part of marine fish identified as abundant, cheap potential source of biodiesel. In this study, discarded fish waste was utilized as low-cost feedstock for biodiesel production. Conventional and microwave irradiation method of lipid extraction were studied for its efficiency. The extracted lipids from fish waste were used for microwave-assisted transesterification in the presence of KOH catalyst and methanol as a green conversion approach.

S. Fimbriata- A Glance



S. fimbriata is one of the major fish varieties, high in its nutritive value form a major fishery resource among the marine pelagic fin fishes of the Indian seas. Fishes plays an important role in the diet of human beings since it is a good source of animal protein. Fish proteins are highly digestible and have high biological and growth promoting value. Proximate composition of various fishes has been studied by different authors; amongst notable ones are the above. Little attention is paid on the study of this particular aspect since of higher nutritive value and usability. Accordingly fish serves as a good source of quality animal proteins, contains

majority of easily digestible amino acids. The investigation and the work regarding the knowledge about nutritive value of *S. fimbriata* are of commercial importance because it contributes the lucrative fishery.Among the total fish catch in India, 32% are different species of Sardines (CMFRI News letter, 2009). Five species of sardines such as ***Sardinella fimbriata***, *S. longiceps, S. gibbsa, S. albella, and S. clupeoides* are common in the east coast of India. Large quantities of sardines are being dried and supplied to the live stock feed industries (Sablani et al., 2002). It is significant to study the nutritive value of S. fimbriata, because it is preferred by coastal people either in fresh or salted, dried form. Fish drying methods vary from species to species based on the type of end product and its quality requirement.

Preservation Technique:

In some countries, the fish are boiled before being dried. Sun drying of fishes is a traditional practice followed in many parts of the world (Sachithananthan et al., 1985; N'Jai, 1985). It has been observed that drying is the most convenient and cheapest method of preservation (Eyo, 1986). Major problems with traditional sun drying are loss of quality due to contamination due to infestation by animals. Solar drying and its improved processes minimize or stop some of the limitations of open sun drying. Drying in solar dryer is different from open sun drying because the solar dryer is an enclosed structure that traps heat inside the drier and make effective use of the heat. Several solar dryer designs have been constructed and tested for different fish species.
The main hypothesis of the present study is to understand the effect of Transesterification on the nutritional composition and microbial quality of sardine and to find out the yield of Transesters an obvious Hydrocarbon.

Another Alternative Potential Source - Micro Algae

Biodiesel production from microalgae is an emerging technology considered by many as a very promising source of energy, mainly because of its reduced competition for land. Among these, especially, microalgae were found to be an alternative nature source of renewable petroleum resources that is capable of meeting the global demand for fuels (Chisti, 2007, 2008). The idea of using algae as a source of fuel is not new (Chisti, 1981; Nagle and Lemke, 1990; Sawayama et al., 1995), but it is now being taken seriously because of the increasing price of petroleum and more significantly, the emerging concern about global warm that is associated with burning fossil fuels (Gavrilescu and Chisti, 2005). It is reported that microalgae can provide several different types of renewable bio fuels which include, methane, biodiesel and bio hydrogen (Gavrilescu and Chisti, 2005; Kapdan and Kargi, 2006; Spolaore et al., 2006). Microalgae have short life cycle and use a photosynthetic process similar to higher plants for their energy. In fact, the biomass doubling time for microalgae during exponential growth is found as short as 3.5 h. Microalgae are veritable miniature biochemical factories, and appear photo synthetically more efficient than terrestrial plant, and are efficient CO2 fixer (Pirt, 1986). The ability of algae to fix CO2 has been proposed as a method of removing CO2 from fuel gases from power plants, and thus, can be used to reduce emission of GHG (Chisti, 2007). Many algae are exceedingly rich in oil, which can be converted to biodiesel. The oil content of some microalgae exceeds 80% of dry weight (DW) of algae biomass (Banerjee et al., 2002; Chisti, 2007). Microalgae are faster in growth in the marine environment and yield of oil from algae is estimated between 5000 to 20000 m3 / 4046 m2/yr which is 7 to 31 times greater than the terrestrial crop, palm oil (635 m3) (Pringsheim, 1950).

OBJECTIVE OF THE STUDY

Due to climatic changes and various other factors includes pollution, Masking of earth crust, fossil fuel depletion is in its thump raise, Hence we rivally should move on to another or stick on to reduced usage. Since the later is impossible the former can be taken in to amount.

REVIEW OF LITERATURE

It can be performed by extractive transesterification reaction involving appropriate ratio of lipid, solvent and catalyst for biodiesel production (Sharma et al., 2014)

Currently, biodiesel is considered as next generation renewable and sustainable fuel produced from plants or animal lipids (Jaiswal and Pandey, 2014)

world is on the brick of energy crisis due to depletion of fossil fuels. The energy and environmental concern spurred the development of low-cost renewable and sustainable fuel resources (Yahyaee et al., 2013)

India is the 2nd largest producer of fish in the world contributing to 5.43% of global fish production due to longest marine coastline of 8,118 kilometers. The fish market and fish processing industry generates enormous quantities of discarded fish waste approximately 1/3rd part such as head, viscera, tail, skin, liver, eyes, fins etc.

which is considered as loss. The marine fish oil extracted from discard part of marine fish identified as abundant, cheap potential source of biodiesel (Patil et al., 2013)

It has been reported various blends of sardine oil biodiesel on the performance and emission characteristics of the diesel engine. The results showed that the specific fuel consumption than diesel for all blends (Narasiman et al. 2012) Non-edible resource can provide an alternative source without competing food uses (Karmakar et al., 2010)

In recent years, researchers have tested microwave energy; a non-conventional heating method for extraction and transesterification of lipids from various feed stocks (Shakinaz et al., 2010)

In the last 10 years, many studies have been conducted on bio fuels for substituting fossil fuels and reduce the greenhouse gas (GHG) emission which is responsible for global warming (Bastianoni et al., 2008)

Biodiesel production from microalgae is an emerging technology considered by many as a very promising source of energy, mainly because of its reduced competition for land. Among these, especially, microalgae were found to be an alternative nature source of renewable petroleum resources that is capable of meeting the global demand for fuels (Chisti, 2007, 2008) used crude tall oil, a by-product in the manufacture of paper pulp, for biodiesel production. The blends of tall oil biodiesel-diesel fuel were tested in diesel engine at full load condition. The engine performance and exhaust emission showed that the engine torque and power output with tall oil biodiesel-diesel fuel blends increased up to 6.1% and 5.9%, respectively as compared to pure diesel oil. The decreased of CO emissions to 38.9% and increased up of NOx emissions to 30% of biodiesel fuel blends were observed (Altiparmark et al. 2006)

It is reported that at higher engine speeds, a slight increase in torque was obtained with the blended fuels and the blend fuel of 30% diesel- 70% biodiesel showed the maximum torque due to the higher cetane number of the blended fuels (Altiparmak et al. 2006) some chemical and physical properties of biodiesel can be affected by oxidation of the fuel during storage (Monyem et al., 2001)

One drawback of biodiesel is that it is more prone to oxidation than petroleum-based fuels and in its advanced stages, can cause acidity in the fuel and form insoluble gums and sediments that can plug fuel filters. Its role as a strategic source of renewable energy in substitution to diesel oil and other petroleum-based fuels (Monyem and Van Gerpen, 2001)

Results from this study revealed that flocculation activity of N. salina and C. marina was higher at pH 11. Similarly, the microalgae B. braunii exhibited maximum flocculation activity at pH 11(Lee et al., 1998)

Fishes normally spoil within 12 – 20 hours depending on the species and the methods of capture. If the fishes are not processed immediately after they are captured, certain irreversible spoilage and deterioration reactions begin to take place (Conne, 1995)

MATERIALS AND METHODS

Sample Collection

About 5 ½ kg of sample (Sardinella fimbriata) that does not meet sales requirement was collected from local fish market , the sample was confirmed with the help of a staff of National Institute of Ocean Technology (NIOT), Chennai, Tamil Nadu, India.

According to muffle statistics Fish and vegetable markets generate garbage of 31 tonnes that constitute 30% of total garbage generated per day of these, waste fishes like Sardinella fimbriata and other related fishes found in large number when compared to other fishes.

Preparation of Fish Oil

3 kg fish waste in the form of a fish head; gills, heart and stomach of fish were washed. After that, the fish waste was added with water as a solvent and it was boiled. The result of boiling fish waste was the oil layer that formed on the upper stew of fish waste. Oil was then taken and put into separation funnel to separate it from the solvent. After the fish oil could be separated with solvent, about 150-200 ml oil was gained. The oil could be used as raw material for biodiesel production or stored in sealed glass bottles.

Lipid Extraction

The total lipid from the fish material was extracted following the method of Folch et al. (1957). The fish material was dried and it was ground with mortar and pestle. Then, chloroform and methanol in the ratio of (2:1) was added to about 500g of minced fish. It was then left undisturbed for 2 hours in the dark. Thereafter it was filtered through a Whatman filter paper (No. 41) and the filtrate was collected in a pre-weighed beaker. The residue was re-extracted in the same solvent (half of the original volume) and filtered in Whatman filter paper (No. 41). Both the filtrates were pooled, and the total volume noted. To the filtrate, $1/5^{th}$ volume of 0.6% saline was added and mixture was transferred to a separating funnel and left undisturbed overnight in the dark. The lower layer was carefully taken out from the separating funnel and allowed to dry.

Evaporation

The mixture was evaporated in vacuum to release chloroform and methanol using rotary evaporator. The beaker (after total evaporation) was weighted again, and the difference indicated the weight of lipid in the fish material.

Mixing of Catalyst And Methanol For Biodiesel Production (National Biodiesel Board, 2002.)

1.75g of NaOH was mixed with 100mL of methanol and stirred properly. The mixture of catalyst and methanol was poured into extracted oil in a conical flask. The conical flask containing solution was shaken for 3hrs by electric shaker at 300rpm. After shaking, the solution was kept for 16 hrs to settle the biodiesel and sediment layers clearly. Biodiesel was washed with 5% water until it became clean.

To 100mL of biodiesel obtained, 900mL of petroleum diesel fuel was added to produce Biodiesel blend (B-10). Then, it was analyzed for finding out certain parameters such as Density, Water content, Kinematic Viscosity, Flash point, Cloud point, Acidity, Copper strip Corrosion test, Ash, Carbon residue, Sulphur content, Calculated Cetane Index (CCI) and boiling point.

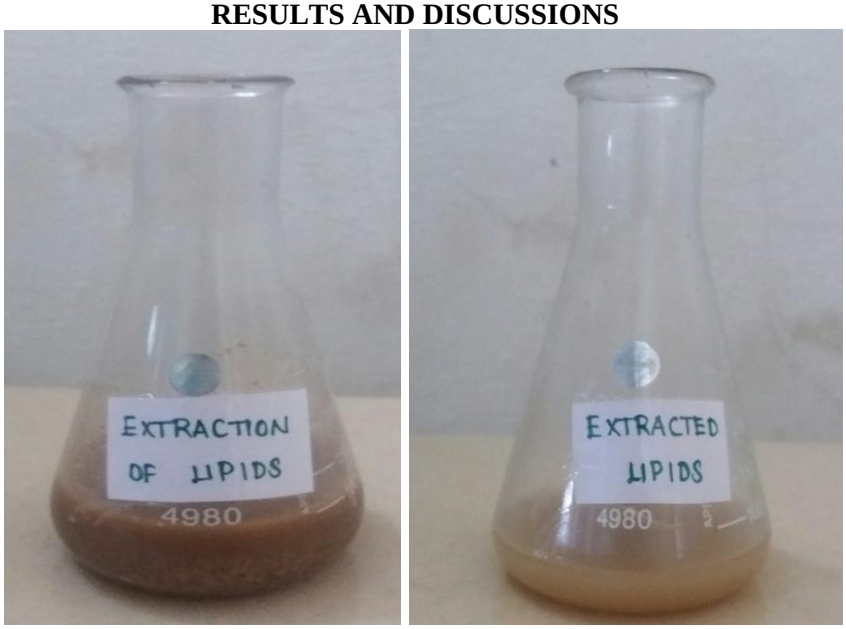
Analysis of Biodiesel

Biodiesel of waste fish oil was determined for its kinematic viscosity, flash point, density, cloud point, conradson carbon residue using ASTM methods and caloric value using Bomb Calorimeter.

Diesel Engine Performance

For this experimental study, biodiesel blends and diesel oil fuels performances were conducted on single cylinder engine, maximum power 2200 rpm, direct injection diesel engine, engine speed changed from 1250 to 1450 rpm, model ER/KND 180 (Kubota).

RESULTS AND DISCUSSIONS



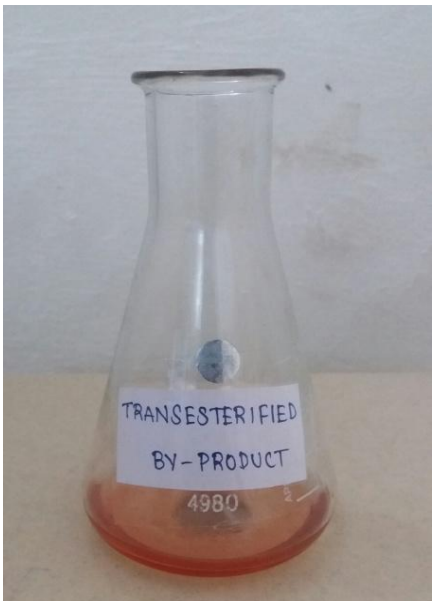


Plate: 1 Production of Biodiesel

Table: 1 Characteristics of Biodiesel

Characteristics of Biodiesel	Waste fish oil Biodiesel	Methods
Kinematic viscosity at 40°C, mm²/s	4.741	ASTM D 445-07
Flash Point P.M., °C	184.5	ASTM D 93-07
Density pada 15°C, g/mL	0.8822	ASTM D 1298
Conradson Carbon Residue, %wt.	0.0016	ASTM D 189-07
Caloric Value, cal/g	9713	Bomb Calorimeter

Characteristics of Biodiesel

The waste fish oil biodiesel characteristic was determined using ASTM method. The characteristic properties of biodiesel as a fuel was determined including kinematic viscosity, flash point, density, conradson carbon residue, caloric value.

Density

The density, or more precisely, the volumetric mass density, of a substance is its mass per unit volume. The symbol most often used for density is D. Mathematically, density is defined as mass divided by volume.

$D = m/v,$

Where D is the density, m is the mass, and v is the volume.

THE DENSITY OF WASTE FISH OIL BIODIESEL: 0.8822 G/ML

Kinematic Viscosity

Kinematic Viscosity is the ratio of absolute viscosity to density, a quantity in which no force is involved. Kinematic Viscosity can be obtained by dividing the absolute viscosity of a fluid with the fluid mass density.

THE KINEMATIC VISCOSITY OF WASTE FISH OIL BIODIESEL: 4.74 MM²/S

Conradson Carbon Residue

Conradson Carbon Residue commonly known as “Concarbon” or “CCR” is a laboratory test used to provide an indication of the coke-forming tendencies of oil. Quantitatively the test measures the amount of carbonaceous residue remaining after the oils evaporation and pyrolysis.

BIODIESEL HAD A LOWER CONRADSON CARBON RESIDUE: 0.0016 WT%

Flash Point

The flash point is the lowest temperature at which vapors of a volatile material will ignite, when given an ignition source. The flash point may sometimes be confused with the auto ignition temperature, which is the temperature at which the vapor ignites spontaneously without an ignition source.

THE FLASH POINT OF BIODIESEL FISH OIL WAS HIGHER: (184.5 °C)

Calorific Value

The amount of heat released by a unit weight or unit volume of a substance during complete combustion. It is also called as "calorific power". This is now usually expressed in joules per kilogram.
The calorific value of biodiesel is between 9-13% which is lower than the calorific value of diesel

DISCUSSION & CONCLUSION

Oil from fish waste can be used as raw material for biodiesel, the process of which is carried out in two stages. The first stage is the esterification process with an acid catalyst (H2SO4) to lower the acid value oil and the second one is transesterification process with alkaline catalyst (NaOH) to change the oil into biodiesel. The optimum conversion of 66.09% was obtained at temperature of 60 ° C for 4 hours, the stirring speed of 600 rpm. The biodiesel produced can be applied to diesel machine with optimum mix of B25 (Biodiesel 25% and Solar 75%). The viscosity values of waste fish oil was 4.71 mm2/s. The flash point values of waste fish oil biodiesel was 184.5 °C. The density of 0.8822 g/ml was obtained from waste fish oil. Waste fish oil biodiesel blends fuel have higher torque and power compared to those diesel oil. Waste fish oil biodiesel blends fuel has lower Brake Specific Fuel Consumption compared to that diesel oil.

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