

Biodiesel Fuel Production by Methanolysis of Fish Oil Derived from the Discarded Parts of Marine Fish

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Abstract-The world is on the brink of energy crisis. The limited fossil fuel sources are unable to fulfill increasing energy demand. The depletion of fossil fuels and augmentation of environmental pollution have led to exploration of alternate fuels. Biodiesel (mono alkyl esters) synthesized from various vegetable and animal fat oils have proven as a potential resource and shown neutral effect on environmental pollution. Most research on biodiesel has focused on using plant based oil as feed stocks. There has been much less research on converting animal based oil into biodiesel. It has been estimated that over a million tons of fish by-products are generated from fishing industry. Some of these products are converted into fish meal and oil, but approximately 60% are not utilized. The major fish by-product includes fish head, viscera and some frame with oil stored in the head. Fish by-product can also be converted into hydrolysis-state through hydrolysis. The marine fish oil is identified as one such potential source of biodiesel as it can be extracted from the discarded parts of the marine fish which may provide an abundant, cheap and stable oil source. The present work emphasizes the synthesis of methyl esters from high free fatty acid marine fish oil and the optimization of process variables like volumetric ratio of oil to methanol, catalyst percentage, reaction time and temperature is done for the highest conversion efficiency by volume.

Key words- Free fatty acid (FFA), Marine fish oil, Transesterification, Biodiesel, Methanolysis, Properties, Characterization

1. INTRODUCTION

In view of escalating energy crisis and environmental degradation, biodiesel is proved to be one of the sources of replacement of petrodiesel, thereby reducing country's dependence on the importing of crude petroleum. Biodiesel satisfy the major requirement necessary for a diesel engine fuel, their suitability as alternative to diesel fuel have been a topic of research. However, their higher viscosity and storage ability issues restrict their direct use as alternative fuels.

The use of vegetable oil in IC engine dates back to 1900 when Rudolf Diesel, the inventor of compression ignition engine used peanut oil as an engine fuel. The oil crisis in 1973 triggered numerous studies on natural oil and fats all over the world but were really entered the field only on 2nd August 1990, the day the Gulf crisis began. Today, 40 years later approximately more than 100,000 cars running on biodiesel in mainly Germany, Sweden and Netherlands and some other countries, representing possibly over 90% of today's cars powered by next biodiesel.

Georing CE et al [1] conducted experiment on eleven straight vegetable oils like castor, corn, cotton seed, crambe, linseed, peanut, canola, safflower, sesame, soybean and sunflower and evaluated their properties as fuel and then compared with diesel and found that all vegetable oils are much more viscous, more prone to oxidation and higher cloud and pour points. It was also found that except for castor oil there was a little difference between gross heat content of any of these vegetable oils. Prasad CMV et al. [2] conducted experiments on non-edible vegetable oils and observed major differences with diesel fuel like higher viscosities, moderately higher densities, lower heating values and possibilities of thermal cracking at the higher temperatures during injection,

Which often result in poor atomization, coating tendencies, carbon deposition and wear? He concluded in his report that high viscosity of the vegetable oils cause problems in the injection process leading to an increase in smoke levels and volatility of the vegetable oils resulting in oil sticking of the injector or the cylinder walls, causing the deposits formation which interferes with the combustion process.

Transesterification, paralysis and emulsification, among these transesterification is the key and foremost important means to produce cleaner and environment friendly fuel from vegetable oils [3]. The transesterification process has been proven world wide as an effective means of biodiesel production and viscosity reduction [4].

Freedman et al.[5] Alkaline metal alkoxides (as CH₃ONa for the methanolysis) are the most active catalysts, since they give very high yields (> 98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%). However, they require the absence of water which makes them inappropriate for typical industrial processes and he also found that a 30:1 molar ratio of methanol to soyabean oil with 1% sulphuric acid gave higher conversion after 44hours of heating at 60°C, they emphasized that if vegetable oils have more than 1% free fatty acids, the acid catalysis become more effective than alkali catalyst.

Ramadhas et al.[6] developed a double stage process for producing biodiesel from high free fatty acid rubber seed oil in which crude rubber seed oil was treated with 0.5% sulphuric acid along with 200 ml methanol per litre of crude oil in the first step for reducing the FFA to about 2% followed by alkaline catalyzed transesterification in second stage. They found that excess addition of acid often darken

the product. The maximum ester conversion was achieved at the reaction temperature of $45\pm 5^\circ\text{C}$ and the viscosity of the biodiesel was nearer to diesel. Lu et al. [7] have described two step process consisting of pre-esterification and transesterification process to produce biodiesel from crude *Jatropha curcas* L. oil. The effects of the methanol/oleic acid molar ratio, reaction time, temperature and catalyst amount on the conversion of the pre-esterification reaction were investigated. Temperature is found to influence the reaction rate. Higher yield was obtained at a higher temperature between 35°C and 65°C . The conversion increased with reaction time. The first 15 minutes is the fastest period of the reaction, in which a conversion of 90% is possible. The yield of biodiesel by transesterification was higher than 98% in 20 minutes of reaction time using 1.3% KOH as catalyst, and a molar ratio of methanol to oil of 6:1 at 64°C . L.M. Das et. Al. [8] has developed triple stage transesterification for producing biodiesel from high FFA Polanga oil and compared with *Jatropha* and *Karanja* were optimized in two stages. It has been also found that the conversion efficiency is strongly affected by the amount of alcohol. The volumetric ratio of 11:1, 11.5:1 and 12:1 of alcohol favors the completion of alkali catalyzed transesterification process within 2h for the formation of JOME, KOMe and POME, which is sufficient to give 93%, 91% and 85% yield of ester, respectively.

It has been estimated that over a million tons of fish by-products are generated from fishing industry. Some of these products are converted into fish meal and oil, but approximately 60% are not utilized. The major fish by-product includes fish head, viscera and some frame with oil stored in the head. Fish by-product can also be converted into hydrology-state through hydrolysis. Hydrolysis involves multiple enzymes and heat treatment to breakdown proteins in to smaller peptides. The final hydrolysates product is usually stabilized by acidification and can be used as fertilizer or as feed ingredients. Hydrolysates of fish by-product contain a significant amount of oil, which can be extracted or converted into biodiesel.

Fish oil, which is composed primarily of unsaturated fatty acids and is particularly rich in polyunsaturated fatty acids (PUFAs), can be used as raw oil for biodiesel production to improve fuel flow fluidity at low operating temperatures. Biodiesel fuels produced from raw oil with longer chain fatty acids generally have a higher cetane number and thus superior compression ignition characteristics [9]. The ignition quality of a diesel fuel is also affected by the degree of saturation of the fatty acid compounds, with a greater saturated fatty acid content resulting in superior ignition quality [10]. Crude fish oil that was extracted from a mixture of waste parts of marine fish was used as the raw material to produce the biodiesel with the maximum conversion efficiency by volume.

2. MATERIALS AND EXPERIMENTAL PLAN

Materials

Crude marine fish oil was procured from Blue line foods (India) Pvt. Ltd which was extracted from the discarded parts of marine fish like viscera, fins, eyes, tails etc., known as soap stock. The chemicals: Methanol, Orthophosphoric acid (99.8%), Sulphuric acid (99.8%), of sd fine chemicals and KOH (98 %) of Karnataka fine chemicals Ltd., are used.

Experimental Plan

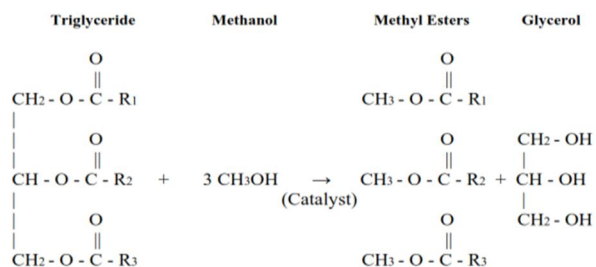
The stirring speed of was kept constant throughout the experiments. The volumetric ratio of oil to methanol was varied in different steps. Catalyst % is varied for each step methanol % variation. Reaction temperature is varied from 40°C to 60°C in steps of 5°C and reaction time is varied from 45min to 180 min for maximum yielding steps with the acid number under the limits. Each batch coded with their batch code, shows the percentage of methanol and catalyst added. Then their properties were measured and tabulated.

3. EXPERIMENTAL SETUP AND PROCEDURE FOR THE PRODUCTION OF BIODIESEL

3.1 Refining and analysis of crude marine fish oil

The expelled crude fish oil contained various impurities such as water, fish residue, saline compound etc., hence, it was refined by a set of 10 micron and 4 micron filter papers, heated for about 1hr at 100°C and then cooled to room temperature by closing the vessel to avoid re-attack of moisture from environment, then stored in PVC cans.

Vegetable oils are water insoluble, hygroscopic substances of plant and animal origin. The vegetable oils are composed of triglycerides; the chemical structure is shown in scheme 3.1, where 'R' represents long chain of hydrocarbons known as fatty acids. The R may be same or vary in chain length and number of double bonds depending upon the particular oil. Free fatty acids play vital role during the production of biodiesel. The FFA more than 2% decreases the yield of the final product. Therefore the acid number and FFA content were measured. Acid number is defined as the number of milligrams of KOH required to neutralize 1gm of oil. This is determined by the standard titrimetry.



Scheme 3.1 Chemical structure of triglyceride

3.2 Experimental setup

Biodiesel from marine fish oil was produced in the laboratory scale set up (Fig.1) consisting of reaction flask with condenser, digital rpm for controlling the magnetic stirrer. The volume of the glass reactor capacity was 2 litres, consisted of three necks, one for condenser and two for monitoring temperature and reactant inputs. A simple mercury thermometer is used to measure the reaction temperature.

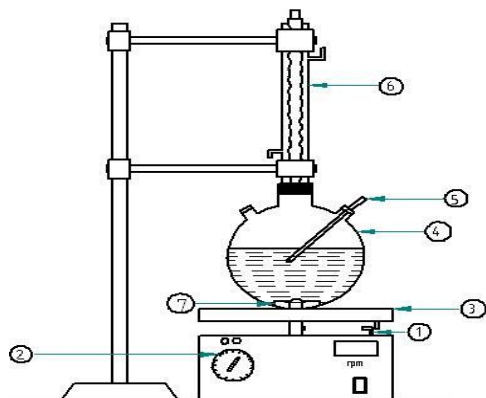


Fig 1 Transesterification Setup

1.rpm sensor, 2.Rheostat for controlling temperature, 3. Hot plate
4.RB flask, 5.Thermometer, 6.Condenser 7.Magnetic bead

3.3 Process optimization for biodiesel preparation from refined marine fish oil in lab scale

It is reported that, in the presence of high FFA content in the oil, transesterification could not take place properly and it also results in the soap formation during the water wash, which decreases the final yield of biodiesel. In the course of test, it is observed that fish oil having high acid number processed in the presence of sulphuric acid catalyzed transesterification, consumed higher amount of acid to decrease the acid number but with the increase in acid catalyst percentage resulting in darkening of final product. Hence, the following stages were adopted for the production of biodiesel to get maximum yield.

3.3.1 Mild acid catalyzed transesterification

The first stage removes organic matter and other impurities present in the oil in the presence of orthophosphoric acid, used as a reagent. Fish oil extracted from the marine fish stock containing the impurities in high quantity, which were causing 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. The orthophosphoric acid is increased in the steps of 0.1% (0.2 to 0.6% v/v) for each step of methanol volume increment in steps of 5% (started from 20% v/v). The reaction temperature is varied from 45°C to 55°C with the steps of 5°C and the reaction time in the steps of 15 minutes. The acid number of the oil settled is measured and taken for the second stage.

3.3.2 Strong acid catalyzed transesterification

The second stage reduces the FFA content present in the oil in the presence of anhydrous sulphuric acid, used as a catalyst. The first stage product is reacted with the sulphuric acid and methanol. The sulphuric acid is varied in the steps of 0.1% v/v for each step of methanol increment in the steps of 5% v/v. The reaction time and temperature were varied for each reaction then; reaction product is

allowed to settle. The FFA and the other impurities were removed in this stage as an upper layer and oil in the lower layer. The acid number of the oil is measured and taken for the third stage.

3.3.3 Base catalyzed transesterification

The settled lower layer of the earlier stages having low FFA is used as a raw material for this stage. The product of earlier stages i.e. pure triglycerides is made to react with methanol and catalyst, KOH. Reactants and reaction time and temperature are varied to achieve the maximum yield. The reacted product of this third stage is made to settle down under gravity. The lower contains the glycerol and other impurities are separated from the methyl esters. The methyl esters were washed with the water to remove the excess alcohol and other impurities present in methyl esters (biodiesel) after the pH neutralization. The separated methyl esters were heated at 100°C to remove the moisture.

4. RESULTS AND DISCUSSIONS

4.1 Composition of Marine fish oil

The physico-chemical properties of the refined marine fish oil are listed in Table 1. The process of production and yield of esterification depends on the free fatty acids, yield considerably decreases if the percentage is more than 2 or acid number of 4, which was determined by titration with 0.01 N KOH. The percentage composition of FFA was also analyzed by gas chromatography it is approximately found to be half of the acid number.

Table.1. Properties of Refined Marine fish oil

I. No.	Properties	Value
1	Specific gravity	0.929
2	Kinematic viscosity at 40°C(cst)	23.2
3	Flash point(°C)	218
4	Fire point(°C)	236
5	Acid Number mg KOH /g oil	34
6	FFA %	17

4.2 Triple stage transesterification

In the course of test, it is observed that fish oil having high acid number processed in the presence of sulphuric acid catalyzed transesterification, consumed higher amount of acid to decrease the acid number but with the increase in acid catalyst percentage, resulting in darkening of final product. Hence, it is processed through all the three stages. It has been optimized the first stage with oil to methanol volumetric ratio of 30:1 and 0.6% v/v of

orthophosphoric acid as reagent with the reaction duration 1.5hr at a temperature of 55°C, has resulted with the acid number of 10.48 mg KOH/g i.e. 5.24% of FFA. The FFA is more than 2%, the extra FFA is converted in to triglycerides in the second stage which has been optimized with the 0.6% v/v of sulphuric acid, oil to methanol volumetric ratio of 20:1, reaction duration of 1.5 hr. The experiments conducted for base catalyzed transesterification that the oil to methanol volumetric ratio of 12:1 and 0.6% w/v of KOH is found to give the maximum conversion of 97.2% at 60°C with the reaction duration of 2hr. Optimized results for the production of biodiesel from the oils are shown in **table 2**.

Table 2. Optimized results for the production of biodiesel from marine fish oil

Sl. No.	Parameters	Marine Fish oil		
		1 st stage	2 nd stage	3 rd stage
1	Oil(ml)	500	560	524
2	Methanol(ml)	150	100	60
3	Orthophosphoric acid(ml)	3	-	-
4	Sulphuric acid(ml)	-	3	-
5	Potassium hydroxide(gm)	-	-	3
6	Reaction temperature(°c)	55	50	60
7	Reaction time(hr)	1.5	1.5	2.0
8	Stirring speed (rpm)	400	350	450
9	Settling hour	2	2	10
10	Water wash and settling hours	-	-	20
11	By product (FFA+Methanol+OM)(ml)	90	136	-
12	Acid number	10.48	2	0.7
13	FFA%	5.24	1	0.35
14	Methanol recovered (ml)	125	100	-
15	Glycerol (ml)	-	-	45
16	Yield (ml)	560	524	486
17	Yield%(v/v)	112%	104.8%	97.2%

4.3 Effect of volumetric ratio of oil to methanol on methyl esters yield

The important parameter that affects the conversion efficiency and production cost is methanol. Stoichiometrically, transesterification reaction requires molar ratio of 3:1 methanol to triglyceride to yield 3 moles of methyl esters and 1 mole of glycerol. But, in practice it is not sufficient. It is observed that longer reaction times were required at lower amounts of methanol. The conversion efficiency of methyl esters during base catalyzed transesterification is studied in this work. The maximum conversion efficiency was achieved at oil to methanol volumetric ratio of 12:1 for fish oil as shown in fig 2. Further increase in methanol amount does not improve conversion efficiency but phase separation become difficult due to higher solubility in methanol. The specific gravity and viscosity decreased with increase in methanol amount.

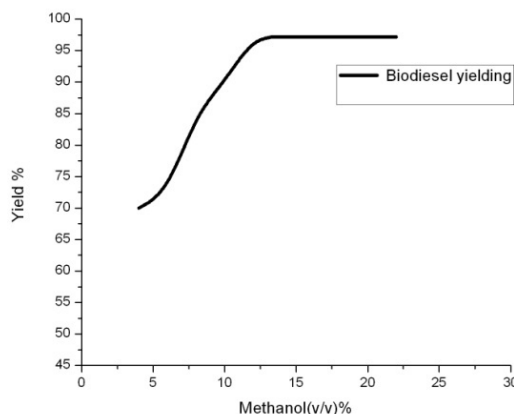


Fig 2 Effect of amount of methanol on yielding during base catalysis

4.4 Effect of amount of catalyst on methyl esters yield

The rate of reaction is faster in the presence of catalyst. During third stage the base catalyst KOH is varied from 0.2% to 1.5% w/v (weight of KOH/volume of oil). The effect of catalyst on conversion efficiency is shown in fig 3. The maximum conversion efficiency was achieved at 0.6% w/v of KOH for fish oil. It is observed that with increase in catalyst percentage reaction duration decreased but at higher amount of catalyst addition yield decreased due to formation of soap or emulsion.

4.5 Effect of reaction duration

During all the reactions stirring speed is kept constant and reaction time is varied between 45 minutes to 3h with the step increase of fifteen minutes. 2h reaction time was sufficient to yield the maximum conversion of methyl esters. It is observed that as the reaction duration increases conversion also increases after that it remains constant as shown in fig 4.

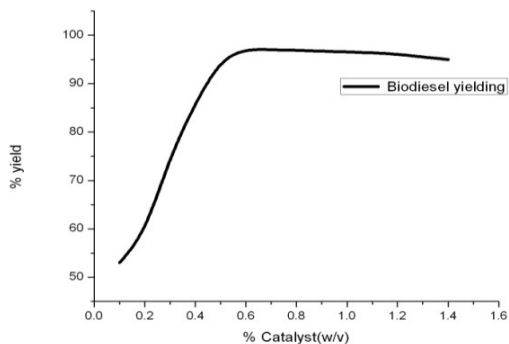


Fig 3 Effect of amount of catalyst on yielding during base catalysis

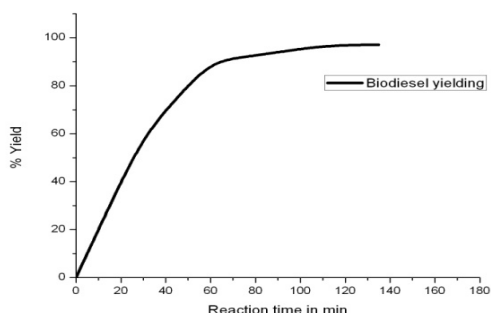


Fig 4 Effect of reaction duration on yielding during base catalysis

4.6 Characterization of biodiesel

The physico-chemical properties of the biodiesel produced from marine fish oil is evaluated as per ASTM standards, experimental methods were followed and results were tabulated in the Table 3.

Table.3 Properties of the Marine fish oil biodiesel

Properties	Test method	Test limit	Fish Oil Methyl Ester
Viscosity , cSt, at 40°C	ASTM D-445	1.9-6.0	4.97
Specific Gravity at 25°C	ASTM D-4052	0.87-0.90	0.888
Calorific Value(KJ/kg)	ASTM D-240	-	40,839
Flash Point(°C)	ASTM D-93	Min.130	152
Fire Point(°C)		-	180
Acid Number (mg KOH/gm of oil)	ASTM D-664	Max 0.8	0.7

5. CONCLUSIONS

In this study, during the production of biodiesel from marine fish oil the following conclusions were derived:

1. The high FFA level of refined marine fish oil can be reduced to less than acid number of 10.48 mg KOH/g i.e. 5.24% of FFA when it is processed through all the three stages. It has been optimized the first stage with oil to methanol volumetric ratio of 30:1 and 0.6% v/v of orthophosphoric acid as reagent with the reaction duration 1.5hr at a temperature of 55°C .
2. The second stage treatment can reduce the FFA level to less than 1% when it is treated with 0.6% v/v of sulphuric acid, oil to methanol volumetric ratio of 20:1, reaction duration of 1.5 hr.
3. The experiments conducted for base catalyzed transesterification on Marine fish oil processed through mild and strong acid catalysis, optimized with oil to methanol volumetric ratio of 12:1 and 0.6% w/v of KOH is found to give the maximum conversion of 97.2% at 60°C with the reaction duration of 2hr.
4. The properties of the biodiesel synthesized found to be within the ASTM standards limits. The viscosity, specific gravity and the acid number were decreased and the calorific value is increased.

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