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Short Communication

# Fast Synthesis of High Quality Biodiesel from 'Waste Fish Oil' by Single Step Transesterification

Yogesh C. Sharma[1*], Bhaskar Singh[2], Devarapaga Madhu[1], Yun Liu[3], Zahira Yaakob[4]

[1]*Department of Chemistry, Indian Institute of Technology (Banaras Hindu University) Varanasi, Varanasi 221005, India.*

[2]*Department of Environmental Science, Central University of Rajasthan, Ajmer 305801, India.*

[3] *College of Life Science and Technology, Beijing University of Chemical Technology, ChaoYang District, Beijing, 100029, P.R.China.*

[4]*Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, Bangi 43600, Malaysia.*

## HIGHLIGHTS

- A waste-oriented economic procedure for biodiesel production.
- High purity biodiesel produced from waste fish oil by a single step transesterification.
- NMR characterization of fatty acid methyl ester (FAME) confirmed high conversion rate (98%).

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## ABSTRACT

A large volume of fish wastes is produced on a daily basis in the Indian sub-continent. This abundant waste source could serve as an economic feedstock for bioenergy generation. In the present study, oil extracted from discarded fish parts was used for high quality biodiesel production. More specifically, a single step transesterification of 'waste fish oil' with methanol using sodium methoxide ($CH_3ONa$) as homogeneous catalyst under moderate operational conditions resulted in highly pure biodiesel of > 98% of fatty acid methyl ester (FAME) content. Characterization was performed by Fourier Transform-Nuclear Magnetic Resonance (FT-NMR).



## 1. Introduction

Biodiesel is globally known as a sustainable alternative fuel for petroleum-based diesel. The advantages delivered by blending biodiesel with diesel are numerous including renewability, carbon neutrality, reduced emission of toxic pollutants and better lubricity of the blended fuel. On the other hand, there are some disadvantages such as comparatively higher emission of oxides of nitrogen, generally higher production cost and less oxidation stability than diesel (Sharma et al. 2008). Despite all these drawbacks, the advantages mentioned earlier are still attractive enough to guarantee the continued production and supply of biodiesel to be used in compression ignition (CI) engines. Numerous attempts have been made to explore potential feedstocks containing substantial oil/lipids which could also lead to economic production of biodiesel. Among those, microalgae, waste cooking oil (WCO) and animal and fish fats/oil waste have attracted a great deal of attention for such resources do not trigger competition with food resources (Sharma et al. 2009). Fish is widely consumed world-wide because of high nutritional value in particular omega-3 fatty acids, eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA). Fish oil has also been found of wide applications such as medicinal uses (Eslick et al. 2009). Around 30-40 % of

* Corresponding author at: Tel.: +91 542 6702865
E-mail address: ysharma.apc@iitbhu.ac.in

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fish is consumed fresh whereas, 60-70 % is being processed for human consumption and other purposes (Eslick et al. 2009). However, not all parts of fish are eaten and substantial parts are discarded. The discarded fish parts include caudal fin, anal fin, pelvic fin, dorsal fin, operculum, overlapping scales, and eye. Therefore, the subcontinent regions worldwide have a vast potential for generation of value added products from fish wastes e.g. waste fish oil. In reality however, the waste fish parts are usually discarded and considered to be of low utility and thus are found of limited applications. Yahyaee et al. suggested various ways for the conversion of discarded fish parts or in another word fish wastes into valuable products such as biodiesel, manure compost, biogas, and energy generation. Chakraborty et al. (2011) used the scales of *Labeo rohita* for preparation of heterogeneous catalyst for transesterification of soybean oil. The fish scales consisting of hydroxyapatite were transformed into β-tri-calcium phosphate when calcined for 2 h at > 900°C. Yahyaee et al. also reported that biodiesel produced from waste fish oil has the potential to replace 5% of the total diesel fuel consumption in the transportation sector in Iran.

This was in line with the report by Andersen and Weinbach (2010) who also implied that biodiesel production from waste triglycerides obtained from poultry and fishing industry could play a significant role in the biodiesel industry worldwide. For instance, the total amount of fish produced in Norway stood at 3568 kilotonne in 2008 and since not all parts of the fish are eatable, Andersen and Weinbach estimated that fish wastes generated in Norway would be more than 1000 kilotonne.

Behcet (2011) tested the performance of the biodiesel obtained from waste anchovy fish in neat form and blended at various ratios with petroleum based diesel (25:75, 50:50, 75:25). Neat biodiesel from the fish oil and those blended with diesel at various proportions showed reduced engine torque by 4.14 %, reduced engine power by 5.16 % and increased specific fuel consumption by 4.96 %. On the advantageous side, the average reductions in exhaust emissions were significant (4.576, 21.3, 33.42 % reduction in $CO_2$, CO and hydrocarbons, respectively, as compared to mineral diesel). Moreover, the anchovy fish oil contained significant amount of saturated fatty acids (37.93 %) that led to improvement in cetane number and resulted in lowered $NO_x$ emission as well. Fish oil also contains a considerable amount of unsaturated fatty acids that improves the low temperature properties of the oil e.g. cold filter plugging point (Lin and Li, 2009). Lin and Li, 2009 reported that palmitic acid (C16:0) and oleic acid (C18:1) were the major components present in mixture of marine fish oil. Biodiesel from the marine fish oil was reported to posses 19.61 and 20.94 % of palmitic acid and oleic acid, respectively (Behcet 2011). Moreover, Hong et al. (2013) argued that biodiesel produced from fish oil had a higher heating value compared to than those of animal fat or vegetable oil.

The present work was set to establish a single step transesterifiaction process for high quality biodiesel production from waste fish oil. Fourier Transform-Nuclear Magnetic Resonance (FT-NMR) was employed to investigate the quality of the fuel generated.

## 2. Experimental

Various discarded fish parts were collected from a local fish market in Varanasi, India. The oil was initially expelled using a mechanical expeller followed by solvent extraction using n-hexane. The fish oil was used for transesterification without any further treatment. Although the stoichiometric ratio for transesterification reaction is 3:1 alcohol to oil molar ratio but experiments have shown that a molar ratio ranging from 6:1 to 12:1 would result in the most optimal transesterification of triglycerides into FAME (Sharma et al., 2008). Using homogenous catalyst, it has been observed that 1 wt % of catalyst is optimal for the transesterification of triglycerides (Sharma et al., 2008). Practically, 25 ml of the waste fish oil was mixed with 1 wt % of catalyst ($CH_3ONa$). Based on our earlier work on used frying oil, 40 vol.% of methanol was considered as an optimum amount for transesterification (Sharma et al., 2012). During the optimization in the present study, the same volume ratio of methanol to oil was found to be optimum to obtain maximum yield of biodiesel from waste fish oil as well (data not shown).

Therefore, 40 vol. % of methanol (i.e. 10 ml) was added to the feedstock and the contents were heated and stirred (1000 rpm) simultaneously at 60 °C for 1 h. The products were kept in a separating funnel and a clear separation of biodiesel and glycerol was observed. The estimation of conversion of oil to FAME was calculated using Fourier transform-nuclear magnetic resonance (FT-NMR) through the following equation as previously described by Knothe (2001).

$$C = 100 \times (2A_{ME} / 3A_{\alpha-CH2}) \qquad \text{Eq. 1}$$

Whereas C is the conversion of feedstock to FAME, $A_{ME}$ is the integration value of the protons of the methyl esters (the strong singlet peak), and $A_{\alpha\text{-}CH2}$ is the integration value of the methylene protons. Multiplayers 2 and 3 are attributed to the fact that methylene carbon owns two protons and the alcohol (methanol derived) carbon has three attached protons.
The yield of biodiesel was determined by weighing the biodiesel obtained after transesterification. The biodiesel yield (%) was calculated on the basis of the ratio of weight of the biodiesel to the weight of fish oil (initially taken for experimentation) multiplied by 100.

## 3. Results and discussion

The scarcity of feedstocks available at an economic rate has led to the exploration of a variety of feedstocks for production of biodiesel. This has included animal waste, waste cooking and frying oil, microalgae, and waste from discarded portion of edible fish. However, as biodiesel is a bulk commodity, a colossal amount of feedstock will be needed to meet the growing demand for biodiesel as an alternative source of fuel. Waste fish oil can be obtained from commercial markets after the edible portion has been separated from the non-edible one The acid value of the waste fish oil was determined at 2.5 mg KOH/g. Hong et al. (2013) synthesized biodiesel from fish oil and reported the optimized conditions to be 12:1 methanol to oil molar ratio, 2.0 wt % catalysts and 120 min reaction time at 55°C. The biodiesel obtained was reported to comply with the ASTM specifications for biodiesel and possessed a low acid value of 0.20 mg KOH/g, kinematic viscosity of 4.60 cSt at 40°C, with a higher heating value (HHV) of 42.1 MJ/k. Swaminathan and Sarangan (2012) reported that a lower calorific value of 37.80 MJ/kg for biodiesel produced from marine fish oil.

Lin and Li (2009) investigated the performance parameters of a CI engine fueled with biodiesel derived from refined marine fish oil and WCO. They argued that marine fish oil biodiesel resulted in better engine performance. More specifically, biodiesel obtained from marine fish oil possessed a higher gross heating value, elemental carbon and hydrogen content, cetane index, brake fuel conversion efficiency and lower elemental oxygen content. They also indicated that $NO_x$ and $O_2$ emissions were higher in fish oil based biodiesel as compared to the WCO-based biodiesel. The FAME content (biodiesel purity) achieved in the present study was determined at > 98 % using Equation 1 and is depicted in Figure 1. A high biodiesel yield of > 97 % was also achieved. The moderate reaction conditions in the transesterification reaction could lead to low cost production of biodiesel and will be a way forward in the commercialization of biodiesel from fish waste oil as a sustainable and waste-oriented feedstock.

As presented in Figure 1, the characteristic peaks of biodiesel were observed at chemical shift of 2.274 to 2.324 ppm in triplet with integration value of 0.96 that was characteristics of α-methylene protons adjacent to carbonyl carbon. A sharp peak of 1.42 was observed during chemical shift at 3.661 ppm which was characteristics of methoxy protons. Other chemical shifts occurred at 5.321, 5.338, 5.356, and 5.387 ppm in form of quaterlet which were characteristics of olefinic protons. A triplet at 2.7 ppm, characteristics of divinyl methylene protons, appeared with an integration value of 0.26. Moreover, a triplet occurred at 1.596, 1.618, and 1.640 ppm with an integration value of 0.92 which was characteristics of β-methylene protons from carbonyl carbon (Swaminathan and Sarangan, 2012 ).
Most studies conducted on the characteristics of fish oil biodiesel only reported physical and chemical characteristics within the ASTM specifications and rarely addressed one of the most important parameter i.e. FAME content. In the present study, no signal was observed in the range between 4.10 to 4.27 indicating complete conversion of triglycerides to FAME. Moreover, the sharp signal observed at 3.661 is characteristics of the formation of high purity biodiesel. Biodiesel obtained in the present work showed FAME content of > 98 % and a high yield (i.e. > 97 %).

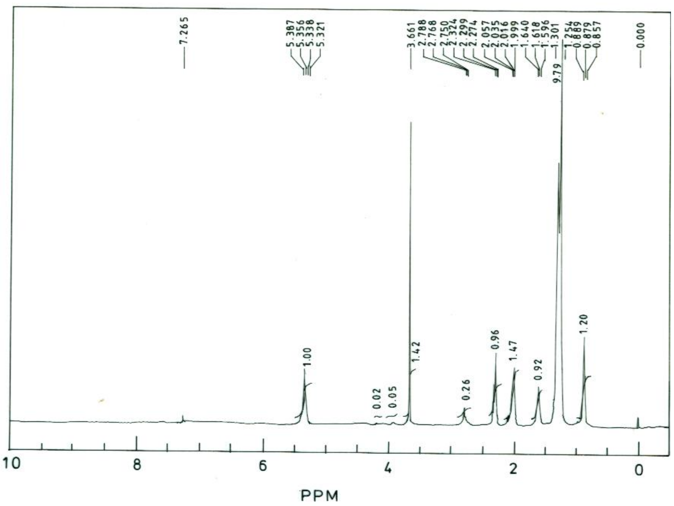

**Fig.1.** 1H NMR of biodiesel derived from the waste fish oil

## 5. Conclusions

A single step transesterification using alkaline catalyst ($CH_3ONa$) performed in the present study showed that the waste fish oil was low in acid value and could be well-used to produce biodiesel of high FAME content. India has a vast coastal area with a colossal consumption of fish. However, in the present scenario, since the fish markets are scattered all over the country, the waste parts are usually disposed of as solid waste with no proper application. Alternatively, these wastes could be channelized into local biodiesel plants as an economic feedstock for high-quality biodiesel production.

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