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# Effect of antioxidants and blending with diesel on partially hydrogenated fish oil biodiesel to upgrade the oxidative stability

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ABSTRACT

Fish oil derived biodiesel has susceptibility to oxidation due to its higher polyunsaturated fatty acid content. Therefore, to control the rapid oxidation process, partial hydrogenation of fish oil biodiesel under 0.5 MPa pressure of $H_2$ by using 0.5% Pd supported on $Al_2O_3$ spherical catalyst was done. It showed 8.0 h of oxidation stability after 1.0 h reaction higher than non-hydrogenated fish oil biodiesel (0.1 h). A decrease in the rate of polyunsaturation (>95%) was achieved after 1.5 h of selective hydrogenation reaction with 17.3 h oxidation stability. Simultaneously, addition of antioxidants, such as3,5-di-tert-butyl-4-hydroxytoluene and tert-butylhydroquinone, to hydrogenated biodiesel was also performed to enhance its induction period more. Hydrogenated biodiesel was further blended with diesel to increase induction period and reduce the pour point. Thus, iodine value, viscosity, acid value and peroxide value of hydrogenated fish oil biodiesel met the EN 14214:2012 standard to be implemented as commercial automobile fuel.

## 1. Introduction

The unbridled growth of world population has given rise to the need for industrialization and urbanization especially for economic solvency and sustainable development. According to BP Statistical Review of World Energy 2020, fossil fuel contributed to 84% of the world's primary energy consumption in 2019 cumulatively (BP, 2020). However, the consumption of naturally found energy sources, such as petroleum, coal, diesel, etc. are leading to the depletion of existing fossil fuel reservations. In addition, the burning of fossil fuel causes air pollution by the emission of greenhouse gases such as carbon dioxide, carbon monoxide, nitrogen oxide, sulfur dioxide, particulate matter and heavy hydrocarbons in the environment from industrial and vehicle exhausts that uses diesel based engines (Hossain et al., 2021a, 2021b), (Singh et al., 2020). The ecosystem and life cycle of humans both are facing risks by these circumstances. Mitigation of the present energy crisis and environmental pollution is giving an incentive to researchers and world leaders to shift towards renewable energy sources. Bio-fuel, more specifically biodiesel, can be a viable replacement for fossil fuels. Biodiesels are advantageous over conventional diesel fuels by their less inflammability, biologically degradability, no or less sulfur content. Hence, biodiesel can be a sustainable and eco-friendly energy source as they have a high octane number and lubricity, low toxicity and a smaller amount of exhaust emission (Chandran, 2020).

Monoalkylated ester of long chain fatty acids named Biodiesel, which is also called fatty acid methyl ester (FAME), is a product formed by the transesterification reaction of triglycerides and alcohol, usually methanol, in the presence of acid or base catalysts (Singh et al., 2020), (Singh and Singh, 2010). The main feedstocks utilized as triglyceride sources are vegetable oils such as soybean, mustard, coconut, canola, sunflower, castor, palm and animal fats like beef tallow, pork lard, chicken fat (Singh and Singh, 2010). However, using edible oil as feedstock can lead to food scarcity and additional use of farming land for oilseeds and thus it increases the biodiesel production cost (Cardoso et al., 2019). Therefore, using oils from non-edible sources and abandoned waste materials such as fat and intestine from the slaughterhouses and fish processing industries can solve the scarcity of feedstock to a great extent. Hence, biodiesel production derived from fish waste extracted oil, also known as fish oil methyl ester (FOME), is much cheaper than other sources. A huge amount of fish waste is produced from fish processing plants which can cause severe environmental damage as the disposal of these wastes are not maintained properly. As there is a possibility of the presence of carcinogenic material and disease transmission through these materials, it cannot be used as poultry or other animal feed either (Fadhil et al., 2017). Hence, extracted oil from fish waste can be one of the most effective and potential biodiesel sources. Though waste fish oil

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derived biodiesel possesses lower kinematic viscosity, lesser emission of harmful gases and great cold flow properties, it has susceptibility to oxidation (García-Moreno et al., 2014).

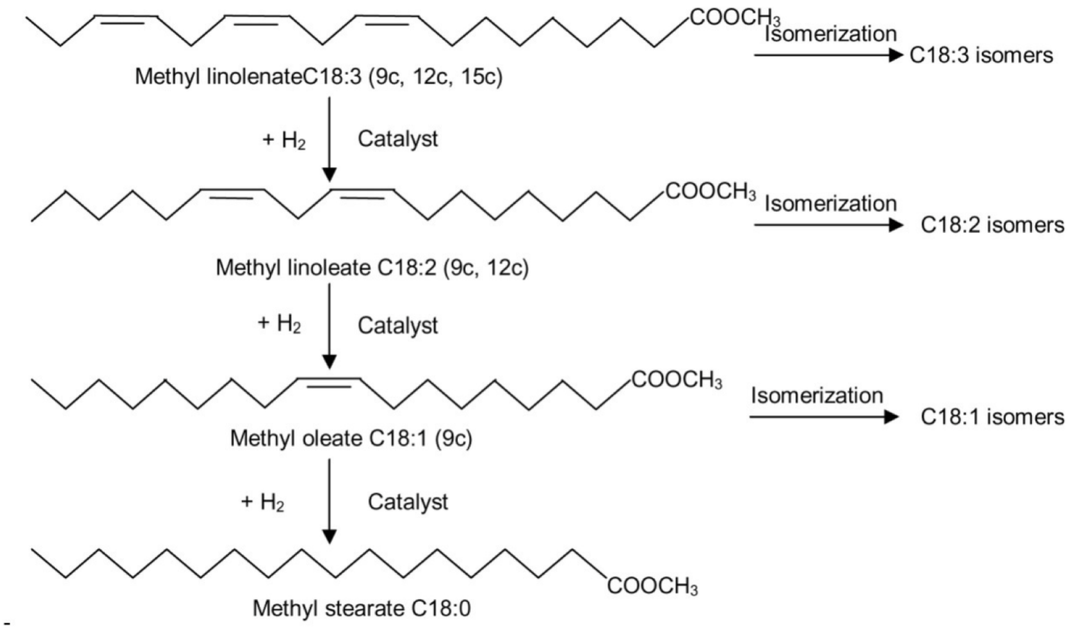
Fish oil contains eicosapentaenoic acid (EPA, C20:5) and docosahexaenoic acid (DHA, C22:6) that covers more than 90% of all Polyunsaturated Fatty Acids (PUFA) (Studentschnig et al., 2015), (Fan et al., 2010). Whereas the amount of higher PUFA (double bonds $\geq$4) has been restricted to the maximum of 12 wt% for methyl linolenate and 1 wt% for methyl esters by European Standards (EN 14214) (Studentschnig et al., 2015). Excess PUFA present in FOME causes lower oxidation stability that can change the biodiesel properties by generating undesirable aldehydes, ketones, peroxides and acids. As a result, total acid number and kinematic viscosity start to increase leading to the difficulty of storage of FOME for a longer period. Conversely, the cold flow properties of FOME, as portrayed by pour point (PP), cloud point (CP) and cold filter plugging point (CFPP), deteriorates with the increase of saturated fatty acid (Adu-Mensah et al., 2019). As the high content of CP, PP and CFPP causes poor engine quality and higher pollutant emissions at low temperature conditions, biodiesel faces crystallization (Leng et al., 2020). Partial hydrogenation of FOMEs as depicted in Scheme 1. can improve these two important fuel properties by converting PUFA into monounsaturated and saturated fatty acids (Adu-Mensah et al., 2019), (Quaranta and Cornacchia, 2020).

In this work, 0.5%Pd supported on $Al_2O_3$ spherical catalyst was used in partial hydrogenation to produce upgraded biodiesel from waste fish oil. There are some published reports of adopting partial hydrogenation to transform cis- FAMEs into trans- FAMEs(Mei et al., 2017)for retarding the rapid oxidation of biodiesel. For the upgrading of oxidative stability of biodiesel- blending biodiesel with diesel, blending of multiple biodiesel, partial hydrogenation of biodiesel (Hazrat et al., 2021), etc. are some mentionable processes taken by the researchers. However, the present study discusses the inclusion of all of these techniques to the produced biodiesel. Partial hydrogenation was done for raising oxidation stability and to minimize the sludge formation after oxidation reaction. 8.0 h of oxidation stability was found after 1.0 h hydrogenation reaction which is a much higher value than the non-hydrogenated fish oil biodiesel (induction period = 0.1 h). Using natural and synthetic antioxidants in FOME can increase the induction period which can also be depicted as oxidative stability. There are many published works of using green tea leave extract (Bharti and Singh, 2020), mango seed kernel extract, rosemary and basil (Buosi et al., 2016) as natural antioxidants and also some reports of using 3,5-di-tert-butyl-4-hydroxytoluene (BHT) (Buosi et al., 2016), (Rodrigues et al., 2020), butylatedhydroxyanisole (BHA) (Yang et al., 2017), propylgallate (PG) (Rodrigues et al., 2020), tert-butylhydroquinone (TBHQ) (Nogales-Delgado et al., 2019), (Hossain et al., 2021a, 2021b), ditert-Butylhydroquinone (DTBHQ) (van der Westhuizen and Focke, 2018) as a synthetic antioxidant as well. The reported antioxidants had been used on biodiesels which were produced from sunflower oil, waste cooking oil, safflower oil, camelina oil and tilapia oil. However, adding antioxidants alone is not viable as their consumption rate is very rapid throughout the process. In this study, a very low concentration (25 ppm) of antioxidants, namely (BHT) and tert-butylhydroquinone (TBHQ), was applied on the biodiesel after the partial hydrogenation. The addition of only 25 ppm TBHQ antioxidant had risen the induction period to a great extent. The iodine value of hydrogenated fish oil biodiesel, which indicates the reduction of polyunsaturation, meets automobile fuel standard. To this date, this type of attempt has been rarely discussed in other publications. On the other hand, there are some reported works of biodiesels, produced from Jatropha oil (Nainwal et al., 2015), waste cooking oil (Nainwal et al., 2015), chicken fat (Keihani et al., 2018), almond oil (Akhihiero and Ebhodaghe, 2020), blending with diesel for upgrading the cold flow properties. Therefore, incorporation of hydrogenated fish oil biodiesel with diesel has not been known to report yet to investigate its effect on pour point. Furthermore, adding of antioxidant (BHT and TBHQ) to the partially hydrogenated biodiesel, to the best of our knowledge, has not been reported yet. However, this present work also provides data of mixing diesel (sulfur free and low sulfur with 440 ppm) with hydrogenated fish oil biodiesel to keep its pour point in lower range.

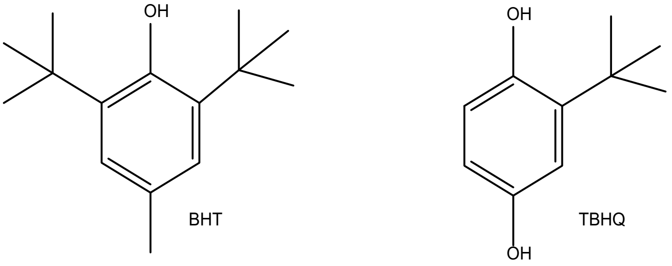
## 2. Methodology

### 2.1. Materials

The fish oil was supplied by Sanki Siryo Co., Ltd., Japan. Two synthetic antioxidants as shown in Scheme 2. i.e., 3,5-di-tert-butyl-4-hydroxytoluene (BHT) and tert-butylhydroquinone (TBHQ) were purchased from Wako Pure Chemical Industries, Japan. The spherical catalyst 0.5% Pd supported on aluminium oxide, which is commonly



**Scheme 1.** Partial hydrogenation of polyunsaturated FAME



**Scheme 2.** Antioxidants used in the present study

used for hydrogenation, was purchased from JGC Catalysts and Chemical Ltd. Japan.

### 2.2. Transesterification of fish oil to FOME

The FFA (Free Fatty Acid) content was measured by performing titration of the fish oil sample against a 0.1 N aqueous potassium hydroxide solution according to standard procedure of EN 14104. The tested sample had FFA value of lower than 2%. Transesterifications were carried out in a separable round bottom reaction flask. Firstly, the oil feedstock was added to the flask and it was then placed onto a heating mantle. Transesterification reaction was carried out with 10:3:0.5 weight ratio of fish oil: methanol: KOH. The reaction temperature was maintained at 65 °C with a magnetic stirrer rotating inside the flask at 600 rpm. Methanol and catalysts were added in different experimental amounts after the temperature of the oil reached to 65 ± 2°Cfor 2 h. After the reaction was completed, the product mixture was taken out of the reactor and glycerol was separated by separating funnel and washed with warm water (60 °C) 5 times for the removal of catalyst and methanol. Finally, fish oil methyl ester (FOME) was distilled at 80 °C for 15 min to remove methanol and water thoroughly.

### 2.3. Partial hydrogenation of fish oil methyl ester

The hydrogenation reaction was carried out in a glass tube auto clave reactor. In a glass tube reactor, 150.0 g of fish oil methyl ester (FOME) was placed and after that 6.0 g of catalyst was added. Then, hydrogen gas flow at 0.5 MPa pressure was given to the reaction medium. After the temperature reached at 120 °C, the hydrogenation reaction started with agitation rate of 1000 rpm and the total reaction time was 2.5 h. The samples were collected every 0.5 h, 1.0 h, 1.5 h, 2.0 h and 2.5 h for the total partial hydrogenation process and analyzed for their pour point, cloud point and iodine value. It was quite difficult to find the optimum condition for the hydrogenation experiment of FOME and all of the isomers could not be identified because many isomers were produced after this process. Hence, the optimum condition was selected by analyzing the cloud point, pour point, color and iodine value.

### 2.4. Analysis of biodiesel fuel

#### 2.4.1. Quantitative analysis of biodiesel composition

GC-FID (column- HP-1, Model-6890 N, Agilent Technology) was used to quantify the biodiesel composition. 5–7 drops of FOME were taken into a vial and diluted with 1.5 ml of tetrahydrofuran (THF). The oven temperature was set to 290°Cand the flow rate of helium as carrier gas was 2.0 ml/min.

#### 2.4.2. Identification of biodiesel composition

The compounds of the obtained biodiesel were identified by GC–MS (Model-6890 N, Agilent Technology). The sample was passed through HP-1 column. Programmed temperature of the oven was 250°Cand 1.0 ml/min flow rate of helium as carrier gas was maintained.

#### 2.4.3. Determination of FOME composition

The composition of fatty acid methyl ester was identified by Agilent 6890 N GC-FID. 5–7 drops of FOME were taken into a vial and diluted with 1.5 ml of THF and passed through HP-88 column. The carrier gas (helium) flowed at a rate of 2.0 ml/min. The set temperature of the oven was 230 °C.

There are three types of major fatty acids, such as saturated (Cn:0), monounsaturated with one double bond (Cn:1) and polyunsaturated with more than two double bonds (≥Cn:2) present in triglyceride molecules (Yaşar, 2020). The fatty acid composition of fish oil biodiesel determined by gas chromatography (GC) has given in Table 1. It is apparent that the biodiesel prepared from fish oil contains about 25.6% of polyunsaturated fatty acid (≥4 double bonds) that includes mainly C18:4, C20:5, C22:5 and C22:6. This is the main cause of poor oxidation stability of the fuel and consequently, it may hamper engine performance. Because increase in the number of double bonds in fatty acid ester triggers the deterioration of fuel stability (Agarwal et al., 2018).

#### 2.4.4. Determination of FOME properties

Tanaka MPC-102A mini-pour/cloud point tester was used to measure the cloud point and pour point. ASTM D6749–02 (2018) for pour point and ASTM 2500-17a for cloud point were followed for the measurement. Acid value was determined by using Metrohm auto-titrator. To measure the free fatty acid content in biodiesel by titration method following EN 14104, 1.0 g of sample was taken. 60 ml of a mixture of 2-propanol and toluene with 1:1 ratio was taken as titration solvent and 0.1 M KOH was used as titrating reagent. Peroxide value was measured by Metrohm auto-titrator. 1 g of sample was taken in a conical flask. Acetic acid (25 ml) and isooctane mixture with a ratio of 3:2 was used as titration solvent. $Na_2S_2O_3$ of 0.1 M was the titrating reagent.CA-200 moisture meter was used to evaluate the moisture content of biodiesel and hydrogenated biodiesel according to EN ISO 12937method. Iodine value of biodiesel fuel and hydrogenated biodiesel fuel was estimated according to EN 14111by titrimetric method. Viscosity of raw material, biodiesel fuel and hydrogenated biodiesel fuel were measured by viscometer according to EN ISO 3104.

### 2.5. Preparation of hydrogenated FOME blend

For the improvement of oxidation stability and to promote commercial use, FOME and hydrogenated FOME (HYD-FOME) were blended with petroleum diesel. Two kinds of diesel such as sulfur free diesel ($S < 10$ ppm) and low sulfur diesel ($S = 440$ ppm) and a model diesel (tetradecane) were used in this experiment. HYD-FOME/diesel mixtures were prepared with different weight ratios, such as 5:95 (B5), 10:90 (B10) and 20:80 (B20) respectively. Pour point and oxidation stability of

**Table 1**
Fatty acid contents of FOME.

| Compounds name | Fatty acid Composition | Content (wt%) |
|---|---|---|
| Methyl laurate | C12:0 | 0.1 |
| Mthylmyristate | C14:0 | 4.5 |
| Methyl palmitate | C16:0 | 17.9 |
| Methyl palmitoleate | C16:1 | 7.1 |
| Methyl heptadecanoate | C17:0 | 1.4 |
| Methyl stearate | C18:0 | 4.7 |
| Methyl oleate | C18:1 | 23.8 |
| Methyl linoleate | C18:2 | 3.3 |
| Methyl linolenate | C18:3 | 1.0 |
| Methyl octadecatetranoate | C18:4 | 1.5 |
| Methyl arachidate | C20:0 | 0.3 |
| Methyl eicosenoate | C20:1 | 5.9 |
| Methyl eicosatrienoate | C20:3 | 1.5 |
| Methyl eicosapentaenoate | C20:5 | 7.5 |
| Methyl behanate | C22:0 | 0.2 |
| Methyl docosapentaenoate | C22:5 | 2.9 |
| Methyl docosahexaenoate | C22:6 | 13.7 |
| Methyl lignocerate | C24:0 | 0.2 |

blended FOME and blended HYD-FOME were measured.

## 3. Results and discussion

### 3.1. *Effect of partial hydrogenation on the composition of FOME*

Hydrogenation proceeded slowly as very low amount of catalyst was used and formation of saturated FOME increased rapidly from 1.5 h in this reaction condition. Fig. 1 shows gas chromatogram of FOME and hydrogenated FOME measured by GC equipped with HP-88 capillary column. Methyl eicosapentaenoate (C20:5) and methyl docosahexaenoate (C22:6) were selectively hydrogenated for 1 h and 1.5 h over $Pd/Al_2O_3$ catalyst because of their higher content than the other polyunsaturated fatty acid methyl esters (≥4 double bonds) present in FOME. However, after this selective hydrogenation, both of the mentioned fatty acid methyl esters got almost vanished as depicted in Fig. 1. As the hydrogenation of polyunsaturated esters occurred rapidly, the total PUFA (≥Cn:4) content is also reduced to 1.25% after 1.5 h of hydrogenation and after 2.5 h of reaction, none of them was found in HYD-FOME. Eventually, the mono-, di- and tri- unsaturated fatty acids faced the same result of reduction. Oleic acid (C18:1) exhibited a significant decrease in amount (wt%) from 25.8% to 1.92% while the saturated molecules (C14:0, C16:0 and C18:0) were increased to a great extent. More particularly, the content of stearic acid (C18:0) was raised from 3.1 wt% to 17.18 wt% because of partial hydrogenation introduction. It may have occurred due to the transformation of cis-isomers into trans-isomers (Sukjit et al., 2019). This phenomenon of increasing saturation rate of FOME made the cold flow properties remain in a satisfactory range in spite of showing a slight elevation in HYD-FOME.

### 3.2. *Fuel properties of FOME and hydrogenated FOME*

Generally, fuel properties of biodiesel include viscosity, cloud point, water content, density, pour point, acid value, iodine value, peroxide value etc. Table 2 is showing the fuel properties of FOME and hydrogenated FOME against the standard values.

The total FAME content of the fish oil biodiesel is 96.7% which is quite satisfactory. But due to the presence of too much polyunsaturated fatty acid (≥4 double bonds), oxidation stability is very low (0.1 h) which is beyond the standard limit following ASTM D6751 (Adu-Mensah et al., 2019), (Knothe and Razon, 2017). The poor oxidation stability of FOME also affected the peroxide value with a relatively high value. Because, peroxide value is directly proportional to the oxidation level of fuel (Lin and Li, 2009). It may have an impact on ignition delay time as ignition delay time decreases with the increase in peroxide value (Pattamaprom et al., 2012). But after hydrogenation of FOME, peroxide value decreased dramatically as illustrated in Table 2. because of the increasing degree of saturation of FOME. This suggested a remarkable upgrade of oxidation stability of FOME after partial hydrogenation from 0.1 h to 8.0 h and 17.3 h and complied with European fuel standard (min 8.0 h) (Mei et al., 2017).

Presence of water in biodiesel is one of the main causes of storage tank corrosion and increase of the formation of soap during transesterification reaction (Cardoso et al., 2019), (Fan et al., 2010) and the biodiesel produced from fish oil showed a considerable value of water content. Though it increased slightly in HYD-FOME than FOME, it did not exceed the standard value (max 530 ppm) (Thanh et al., 2010). Iodine value has exceeded the maximum criteria of 120 as iodine value shows increment with the increases in the number of double bonds (Thanh et al., 2010), (Gopinath et al., 2009). As the degree of unsaturation decreased in HYD-FOME with an increased reaction time of hydrogenation of 1.0 h and 1.5 h, iodine value turned back within the acceptable range of 102 and 100 respectively. The obtained FOME showed an acceptable result of viscosity within range according to European standard. This indicates the ability of preserving the characteristics of biodiesel lubricity (Martins et al., 2015). Although it increased very slightly after hydrogenation, it was considerable. Almost the same type of behavior was reported in some previous works in case of cottonseed oil biodiesel and soybean oil biodiesel (Adu-Mensah et al., 2020), (Mei et al., 2020), (Alexandrino et al., 2013). This may result because of the conversion of any cis-FAME into trans-FAMEs in the final product after hydrogenation (Mei et al., 2020), (Alexandrino et al., 2013). Acid value of any FAME expresses the free acid present in it. The higher the acid value, the higher the probability of formation of an acidic product during oxidation (Agarwal et al., 2018). In the present work, FOME has a considerable acid value that is compatible with the standard limit (maximum 0.5 mg KOH/g) and it even got reduced more after partial hydrogenation (Todaka et al., 2013).

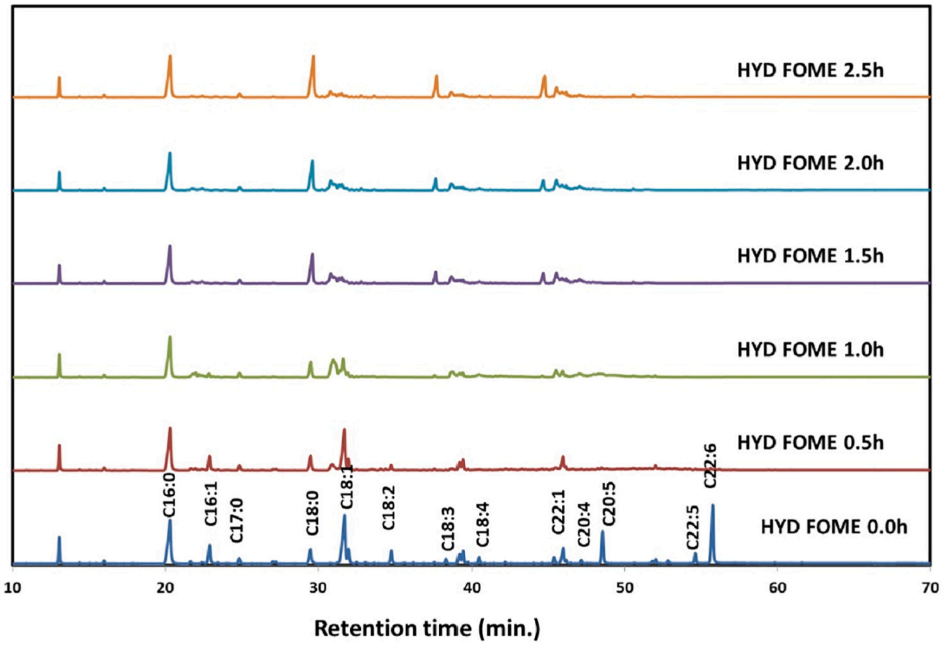


**Fig. 1.** Gas chromatogram of FOME and HYD-FOME.

**Table 2**
Fuel properties of FOME and hydrogenated FOME.

| Parameter | Unit | Test Method | FOME | 1.0 h HYD-FOME | 1.5 h HYD-FOME | EN14214, 2012 |
|---|---|---|---|---|---|---|
| Fatty Acid Methyl Ester | mass % | (a) | 96.7 | (c) | (c) | – |
| Viscosity | mm$^2$/s | EN ISO 3104 | 4.2 | 4.5 | 4.7 | 3.5–5.0 |
| Water Content | ppm | EN ISO 12937 | 430 | 460 | 453 | ≤500 |
| Oxidation Stability | h | EN 14112 | 0.1 | 8.0 | 17.3 | ≥8 |
| Acid Value | mg KOH/g | EN 14104 | 0.25 | 0.07 | 0.05 | ≤0.5 |
| Peroxide Value | meq/Kg | JOCS standard method | 17.92 | 3.0 | 1.52 | – |
| Iodine Value | g I$_2$/100g | EN 14111 | 156 | 102 | 100 | ≤120 |
| Linolenic Acid Methyl Ester | mass% | (a) | 0.9 | (c) | (c) | – |
| Polyunsaturated FAME (≥4 double bonds) | mass% | (a) | 25.6 (approx.) | 1.6 (approx.) | 1.3 (approx.) | – |
| Pour Point | $^0$C | ASTM D6749–02 | 2 | 4 | 8 | (b) |
| Cloud Point | $^0$C | ASTM D2500-17a | 3 | 11 | 18 | (b) |

(a) Values were calculated from the GC analysis using HP-88 column.
(b) Depends on Geography and time of year (Knothe and Razon, 2017).
(c) Not determined.

### 3.3. Effect of antioxidant addition on oxidation stability hydrogenated FOME

After hydrogenation for 1.0 h, induction period of FOME was increased from 0.1 h to 8.0 h and met the biodiesel standard (ASTM D6751). However, it did not comply with the EAS-ERIA biodiesel fuel standard which is minimum 10.0 h (Goto et al., 2010). To achieve the targeted value, addition of small amount of antioxidant to HYD-FOME was examined. In this work, commercially available antioxidants such as TBHQ and BHT were used. The obtained induction period (14.1 h) was more than the standard value after addition of 25 ppm of TBHQ to HYD-FOME. 100 ppm of TBHQ showed induction period of 22.1 h in HYD-FOME. The gradual transformation of induction period with increasing concentration of antioxidants is illustrated in Fig. 2. It is seen that TBHQ showed a better performance than BHT. In a previous study, Rodrigues et al. (2020) reported the use of BHT to tilapia oil biodiesel and found to increase slightly its induction period from 1.98 h to 3.12 h. Again, Nogales-Delgado et al. (2019) reported the higher effectiveness of TBHQ having a high concentration (1000 ppm) than other antioxidants in case of safflower oil biodiesel and improved induction period to 8.0 h. On the contrary, our present work resulted in more than 20.0 h induction period with only 100 ppm TBHQ addition.

TBHQ and BHT, both are phenolic antioxidants and they act as efficient hydrogen donor due to their active hydroxyl group. With the increase of hydrogen in reaction medium, unusual formation of free radical gets restrained in the biodiesel product and thus they prevent the oxidation chain reaction (Maglinao et al., 2020), (Chen et al., 2019). As TBHQ holds more hydroxyl groups than BHT, it can provide more hydrogen to the reaction system than BHT (de Jesus et al., 2020). For these reasons, TBHQ helped more to prevent oxidation of hydrogenated FOME than BHT. Eventually, it is proved that the combination of partial hydrogenation with antioxidant addition is very effective for the improvement of oxidation stability.

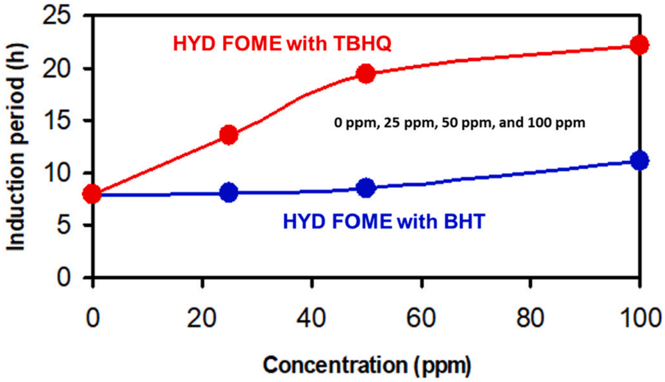


**Fig. 2.** Oxidation stability of HYD-FOME with antioxidant.

### 3.4. Effect of hydrogenation on cloud point and pour point

In case of biodiesel, cloud point (CP) and pour point (PP) are two most important concerns for better engine performance, especially for cold weather regions. If the cloud point and pour point of the biodiesel is higher than the temperature of outside environment, crystallization of fuel occurs. When unsaturated fatty acid content is higher in biodiesel, CP and PP are lower (Hazrat et al., 2020). Because of this reason, the obtained FOME has lower CP and PP as mentioned in Table 2. But after hydrogenation of FOME their value increases. CP and PP of every sample of hydrogenated FOME seemed to increase rapidly with the 2.5 h time period. A higher amount of saturated FAME formation can be attributed for this phenomenon. CP of the samples obtained at 1.0 h and 1.5 h shows higher value than their corresponding PP as shown in Fig. 3. As a large amount of trans isomer formation was observed in between 0.5 h and 2.0 h, it may cause an increase in CP (Adu-Mensah et al., 2019).

### 3.5. Oxidation stability and pour point of hydrogenated FOME blended with diesel

For promoting the commercial introduction of FOME, it was important to blend hydrogenated FOME with petroleum diesel. To clarify the quality of FOME/diesel mixed fuel, the induction period was measured by Rancimat according to biodiesel blended EN temporary standard. The experimental results were shown in Table 3. All the results were reached to 20 h of oxidation stability except 20 wt% hydrogenated FOME/sulfur free diesel and conceded with the standard. Little higher induction period was found in FOME blended with low sulfur diesel (S =

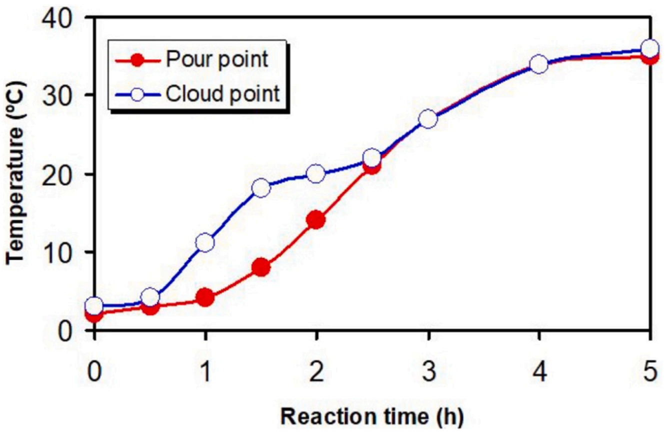


**Fig. 3.** CP and PP of HYD-FOME at different reaction time.

**Table 3**
Oxidation stability of hydrogenated FOME (1 h) blended with diesel.

| HYD-FOME (wt%) | Induction Period (h) | | |
|---|---|---|---|
| | With tetradecane | With sulfur free diesel | With low sulfur diesel (440 ppm) |
| 5 | >24 | >24 | >24 |
| 10 | >24 | >24 | >24 |
| 20 | 22.8 | 16.5 | 21.1 |

440 ppm). According to the literature (San, 2009), sulfur compounds contained in diesel such as benzothiophene act as oxygen trap during oxidation (e.g. benzothiophene is converted to benzothiophene dioxide). So, it is favorable to use high sulfur diesel from the viewpoint of oxidation stability.

Fig. 4 shows the effect of blending on pour point of hydrogenated FOME/diesel mixture. After partial hydrogenation (1 h), pour point of hydrogenated FOME reached to 4 °C from 2 °C. But, it is apparent from Fig. 5. that pour point of HYD-FOME decreased rapidly as it was blended with diesel. Furthermore, pour point of hydrogenated FOME/diesel mixture increased with increasing FOME content from 5 wt% to 20 wt%.

1.5 H hydrogenated FOME was blended with sulfur free and low sulfur diesel and the experimental results are shown in Table 4. All the blended FOME showed more than 24 h induction period that satisfied temporarily the EN B5, B7 and B10 biodiesel standard

As shown in Fig. 5, with the increasing blending ratio of FOME biodiesel to 5 wt%, 10 wt%, and 20 wt% respectively, the value of pour point increased significantly. A similar trend was also found in case of biodiesel blends obtained from chicken fat (Keihani et al., 2018) and almond oil (Akhihiero and Ebhodaghe, 2020) but they failed to obtain pour points below zero. Whereas in the present study, all the values of pour points of the blended samples are below zero and these fuels can be used in cold regions. Below 20 wt% FOME blend, pour point of hydrogenated FOME (1.5 h)/diesel is almost equal to corresponding hydrogenated FOME (1 h)/diesel as depicted in Figs. 4 and 5.

From the experiments, it is proved that blending of partially hydrogenated biodiesel with commercial ones enables to convert low quality fish oil biodiesel into high quality transportation fuel.

### 3.6. *Performance analysis for the effect of partial hydrogenation on FOME*

Partial hydrogenation and catalyst effect on the produced FOME was compared with some other recently published works and discussed in Table 5. Most of the studies reported in Table 5 are mostly based on different catalysts that had been used in partial hydrogenation and the conditions of the reactions were discussed as well. However, Wei et al. (2018) worked with Raney-Ni leading to reduction of unsaturation rate to 35%. Zhu et al. (2021) have also worked with Jatropha oil using Ni/bentonite resulting higher conversion of saturated compounds of 41% in terms of higher temperature of 200 °C. Adu-Mensah et al. (2021) reported decrease in unsaturationrate of only 23% whereas 79% of increase in saturation rate was achieved using high amount (26 g)of Raney-Ni catalyst. Moreover, Adu-Mensah et al. (2021) gained a saturation increase of 54% with soybean oil which was also achieved at the expanse of 26 g of Raney-Ni catalyst. Phumpradit et al. (2020) published a report of up to 80% conversion rate of unsaturation with palm oil using Ni/Sillica ball and Ni/Sillica fibre, with a time period of 4 h of partial hydrogenation, that can be proved to be costly in an industrial setup. In this study, by using only 6 g 0.5%Pd/$Al_2O_3$, the decrease in the rate of unsaturation was up to 95% of the biodiesel prepared from fish oil. The temperature of the reaction was 120 °C and the pressure of $H_2$ was about 0.5 MPa. The saturation rate of the biodiesel was up to 83% after 2.5 h of partial hydrogenation. Thus, the reaction conditions associated with the used 0.5%Pd/$Al_2O_3$ catalyst in this study show remarkable effectiveness in the reduction of unsaturation rate and increase in the saturation rate as well.

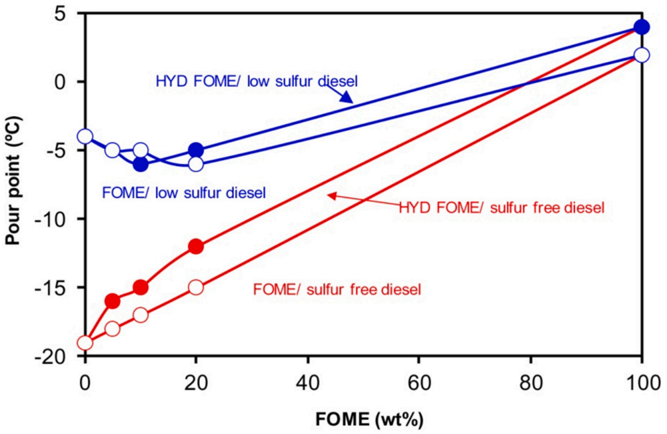


**Fig. 4.** Pour point of FOME and HYD FOME (1 h) with diesel.

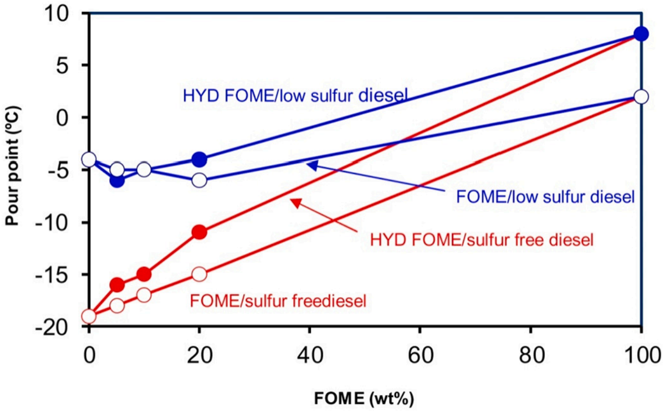


**Fig. 5.** Pour point of FOME and HYD FOME (1.5 h) with diesel.

**Table 4**
Oxidation stability of hydrogenated FOME (1.5 h) blended with diesel.

| HYD-FOME (wt %) | Induction Period (h) | |
|---|---|---|
| | HYD-FOME/ sulfur free diesel | HYD-FOME/low sulfur diesel (440 ppm S) |
| 5 | >24 | >24 |
| 10 | >24 | >24 |
| 20 | >24 | >24 |

## 4. Conclusions

Partial hydrogenation of FOME by 0.5%Pd/$Al_2O_3$ catalyst was effective to improve the induction period (17.3 h). Methyl icosapentaenoate and methyl docosahexaenoate were selectively hydrogenated to oxidative stable saturated esters. Iodine value (100 g $I_2$/100 g) enhanced dramatically with hydrogenation and fulfilled BDF standard. About 25 ppm of TBHQ addition to the HYD-FOME promoted its improvement in oxidation stability (14.1 h). All the blended FOME (B5, B10 and B20) showed more than 24 h induction period in 1.5 h hydrogenation reaction. Additionally, pour points of HYD-FOME/sulfur-free diesel mixtures ($< -7.5$ °C) met Asian diesel standard.

## CRediT authorship contribution statement

**Mosharof Hossain:** Conceptualization, Methodology, Software,

**Table 5**
Performance comparison of fish oil biodiesel by partial hydrogenation and catalysts used.

| Source of Biodiesel | Time of partial hydrogenation | Catalyst used (wt%/ g) | Reaction condition<br>Temperature (°C)<br>Stirring (rpm)<br>Pressure (MPa/ bar) | Rate of increase of Saturation (wt%) (approx.) | Rate of decrease of unsaturation (wt%) (approx.) | Reference |
|---|---|---|---|---|---|---|
| Jatropha oil | 50 min | Raney Ni<br>(6–14 wt%) | 70–90 °C<br>200–600 rpm<br>- | 15 | 35 | (Wei et al., 2018) |
| Jatropha oil | 1 h | Ni/ bentonite<br>(3.33 wt%) | 200 °C<br>400 rpm<br>0.3 MPa $H_2$ | 41 | 9 | (Zhu et al., 2021) |
| Soybean oil | 2 h | Raney Ni<br>(26 g) | 85 °C<br>600 rpm<br>- | 54 | 19 | (Adu-Mensah et al., 2021) |
| Cotton seed oil | 2 h | Raney Ni<br>(26 g) | 85 °C<br>600 rpm<br>- | 79 | 23 | (Adu-Mensah et al., 2021) |
| Palm oil | 4 h | Ni/silica ball (1.97 g)<br>and<br>Ni/silica fibre (0.40 g) | 75–200 °C<br>-<br>1–4 bar $H_2$ | 10 | >80 | (Phumpradit et al., 2020) |
| Palm oil | 5 h | – | 20–60 °C<br>-<br>- | 17 | 16 | (Kongprawes et al., 2021) |
| Corn oil | 4 h | carbonized mistalea<br>(0.1176 g) | 80 °C<br>500 rpm<br>4 bar $H_2$ | Almost no change | Almost no change | (Erenturk and Korkut, 2018) |
| Fish oil | 2.5 h | 0.5%Pd/$Al_2O_3$<br>(6 g) | 120 °C<br>1000 rpm<br>0.5 MPa $H_2$ | > 83 | > 95 | Present study |

Formal analysis, Investigation, Visualization. **Sharmin Sultana Israt:** Validation, Writing – original draft. **Nuzhat Muntaha:** Visualization, Writing – original draft. **Mohammad Shah Jamal:** Writing – review & editing, Visualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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