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Renewable vs. Non-renewable Antioxidants: Comparison between Antioxidant Activity of Ginger Extract and TBHQ for Protecting Biodiesel

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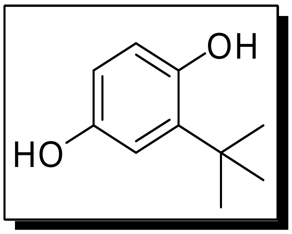
Abstract—*Antioxidant plays a crucial role in protecting biodiesel from degradation. As an option to stop or slowing down the oxidation process, synthetic antioxidants are added to inhibit the initiation and propagation of free radicals, reducing the formulation of secondary degradation compounds. Synthetic antioxidants like TBHQ (tert.-butylhydroquinone) have phenolic compounds therefore they are added to biodiesel to inhibit the radical formation. These synthetic antioxidants are made from non-renewable sources and has carcinogenic health constrains for the living organisms directly exposed to them, because of these negative attributes renewable antioxidant sources containing phenolic compounds are more desirable than the synthetic antioxidants. As a renewable substitute the antioxidant activity of Ginger extract has been compared with TBHQ for enhancing oxidation stability of biodiesel. In this study, a total of 11 treatments of Pongamia biodiesel doped with TBHQ and ginger extract were studied for evaluating the oxidation stability i.e. Pongamia biodiesel containing 0ppm doping (BG_0), Pongamia biodiesel containing TBHQ 100ppm (WA_1), 250ppm (WA_2), 500ppm (WA_3), 1000ppm (WA_4), 2000ppm (WA_5); Pongamia biodiesel containing ginger extract 100ppm (BGX1), 250 ppm (BG_1), 500 ppm (BG_2), 1000 ppm (BG_3), 2000 ppm (BG_4). It has been compared for 180 days storage period in order to promote the use of natural antioxidant for protecting biodiesel. The oxidation stability was determined by professional biodiesel rancimat instrument. The results demonstrated that a minimum doping of 100 ppm of ginger extract in pongamia biodiesel has met both American (ASTM D-6751) and European (ENE14214) standard specification for biodiesel oxidation stability and can be used as antioxidant for biodiesel. The comparative study of antioxidant activity of TBHQ and Ginger extract revealed ginger extract's efficacy in protecting biodiesel and can be taken as an alternative to synthetic antioxidant.*

Keywords*: Antioxidant, ginger extract, TBHQ, Rancimat instrument, oxidation stability.*

1. INTRODUCTION

Renewable fuels are one of the technological issues that became more fascinating due to the environmental benefits. In this context, biodiesel deserve highlight because of its biodegradability and low pollutant emission compared to petro diesel. The key problem associated with the use of biodiesel is its low oxidation stability which affects its storage and makes it unsuitable for engine. The oxidation of the biodiesel primarily increases the peroxide value and then a decrease as primary products degrades to form secondary products. The increase in peroxide value can impart the rise in cetane number, which reduces ignition delay and can cause various engine problems [1].

As an option to stop or slowing down the oxidation process, antioxidants are added to inhibit the initiation and propagation of free radicals, reducing the formulation of secondary degradation compounds. Synthetic antioxidants have phenolic compounds therefore they are added to biodiesel to inhibit the radical formation. Butylated hydroxytoluene (BHT), butylated hydroxyanisol (BHA), tert.-butylhydroquinone (TBHQ) and propyl gallate (PG) are commonly used synthetic antioxidants in biodiesel. These synthetic antioxidants are made from non-renewable sources and has carcinogenic health constrains for the living organisms directly exposed to them, because of these negative attributes renewable antioxidant sources containing phenolic compounds are more desirable than the synthetic antioxidants [2]. In this context, Ginger extract has recently been reported as a nature based robust additive for protecting biodiesel from oxidation. Ginger extract contains phenolic compounds naming gingerol and shoagol which are effective agents for stopping radical propagation. Ginger extract presented greater protection for biodiesel during the oxidation stability test by Rancimat method. A higher percentage of added nature based robust ginger extracts results in the enhancement of the oxidation stability due to the presence of more antioxidant compounds in it. The addition of ginger extract can act as antioxidant and it has been recommended as a natural antioxidant for biodiesel, therefore, it can be added as natural additive to biodiesel. The results demonstrated that a minimum doping of 250 ppm of ginger extract in pongamia biodiesel has met both American (ASTM D-6751) and European(ENE14214) standard specifications for biodiesel oxidation stability and can be used as antioxidant for biodiesel [3].



TBHQ

Here in the present work we are going to compare the Ginger extract and TBHQ for oxidation stability enhancement of *pongamia pinnata* biodiesel to evaluate the efficacy of ginger extract against the synthetic antioxidant TBHQ. The action of synthetic antioxidant TBHQ was monitored by rancimat method and compared with the results obtained for natural antioxidant ginger extract.

2. MATERIALS AND METHODS

2.1. Feedstock used for biodiesel production

Pongamia pinnata is a medium-sized tree grown mostly in the plain humid regions of Assam, lower parts of Meghalaya, Nagaland, and Northern Bengal in India shown in fig.1. It is commonly known as Koroch in Assam, the seeds are shown in Fig. 1. The tree grows to a height of 18-20 m. It bears a seed which is usually harvested from the month of December to March. The oil obtained is pale yellow in color and is non-edible [4].

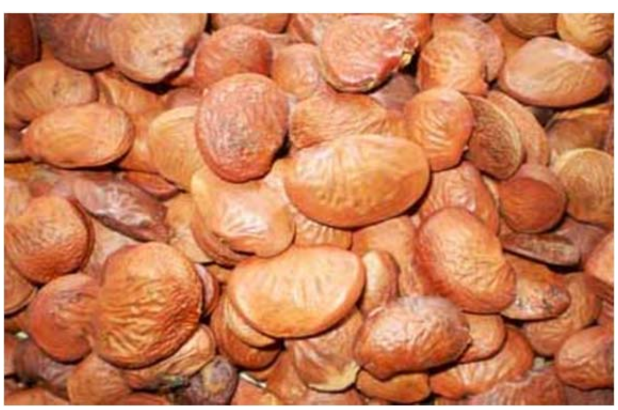


Fig. 1: *Pongamia pinnata* seeds

2.2. Oil extraction from *Pongamia pinnata* seeds

The collected seeds were sun dried and in an oven at 110 °C to remove any traces of moisture. The moisture free seeds were dehulled, kernels removed and grinded using a standard mixture grinder. Oil was extracted by the Soxhlet extraction method using n-Hexane as solvent. The extracted oils were dried over anhydrous Na_2SO_4 and filtered to remove solid particles and impurities and stored in volumetric flasks [5].

2.3. Biodiesel sample preparation

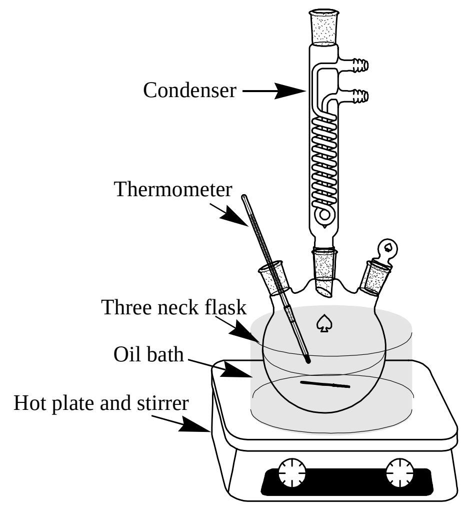


Fig. 2: Schematic representation of the setup for biodiesel production

Pongamia biodiesel was prepared using *Pongamia pinnata* oil via transesterification process involving the reaction of oil with methanol under reflux conditions. The schematic set-up for the synthesis of biodiesel from the *pongamia pinnata* has been given in Fig. 2. The methanol and oil are immiscible so the agitating speed was kept at 600 revolutions per minute (rpm) to ensure efficient mixing. 2wt% of KOH catalyst and 6:1 molar ratio of methanol to *Pongamia pinnata* oil was used and then the contents of the flask were placed at 70 °C for six hours. The mixture was mixed continuously till the completion of the reaction. Then the reaction mixture was poured to separating funnel and allowed to settle. The phases were then separated, upper phase was methyl ester and lower phase contained glycerine. Excess methanol is separated from the mixture using rotary vacuum evaporator. Upper phase i.e. methyl ester (biodiesel) was washed with distilled water several times to neutralise the catalyst along with the removal of glycerine. Finally biodiesel is dried over anhydrous Na_2SO_4 [6].

2.4. Sample preparation for determination of oxidation stability of biodiesel adding TBHQ

Addition of TBHQ in Biodiesel has been shown in Fig. 3. Pongamia biodiesel containing TBHQ 100ppm (WA_1), Pongamia biodiesel containing 250 ppm of TBHQ (WA_2), Pongamia biodiesel containing 500 ppm of TBHQ (WA_3), Pongamia biodiesel containing 1000 ppm (WA_4), Pongamia biodiesel containing 2000 ppm (WA_5) were prepared for evaluating the oxidation stability and the results obtained has been compared with the reports of our previous work where ginger extract has been used as a natural antioxidant for biodiesel. The oxidation stability of these prepared samples was quantified by the induction period (IP). The IP was tested using Rancimat method (EN14112) and ASTM Standard D-6751 at 110 °C. All oxidative stability measurements were carried out on a Metrohm professional biodiesel Rancimat instrument. Fig. 4 has shown the schematic rancimat instrument method. In the Rancimat Method, the oxidation is created by passing an air stream at the rate of 10 L/h through biodiesel sample (3 g), at constant temperature 110 °C. The vapours produced during the oxidation process along with the air, are passed into the flask containing 50 mL of demineralized water, and contain an electrode for measuring the conductivity. The electrode is connected to a device which is responsible for measuring and recording. It indicates the end of induction period when the conductivity begins to increase rapidly. When the conductivity of this measuring solution is recorded continuously; an oxidation curve is obtained whose point of inflection is known as the induction period [7].

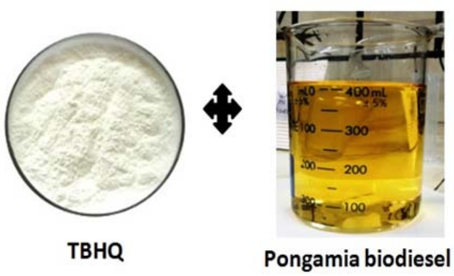


Fig. 3: Addition of TBHQ with Biodiesel

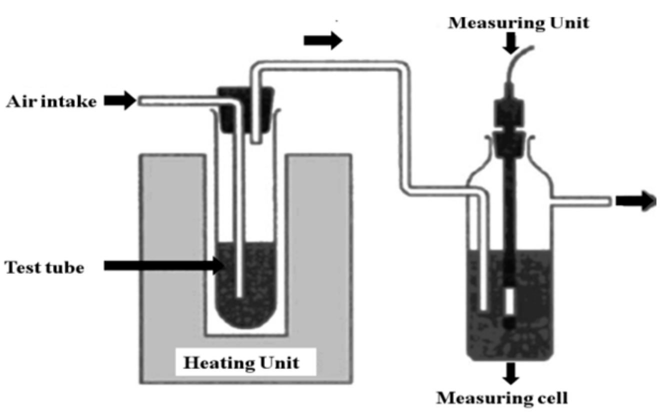


Fig. 4: Schematic representation of Rancimat instrument

The produced biodiesel has been characterized through ^1H NMR and Fig. 5 shows the ^1H NMR spectra of the produced pongamia biodiesel. The peak at 3.6 ppm and 2.3 ppm confirms the conversion of oil into biodiesel [8].

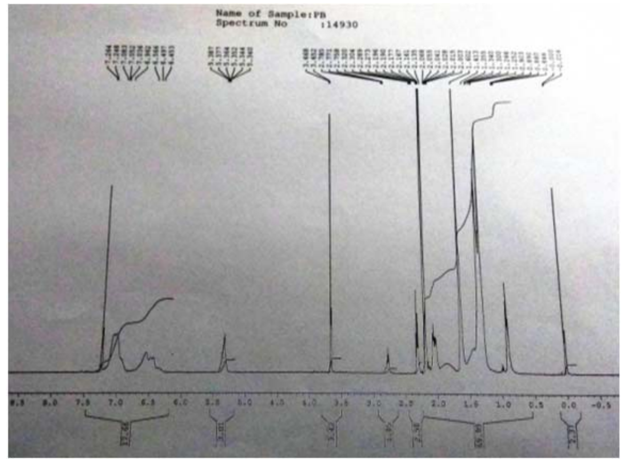


Fig. 5: ^1H NMR of *Pongamia pinnata* biodiesel

3. RESULTS AND DISCUSSION

3.1. Effect of addition of TBHQ on the oxidation stability of Pongamia biodiesel

For the study of effect of addition of TBHQ on the oxidation stability of Pongamia biodiesel, five numbers of samples of *Pongamia pinnata* biodiesel were doped with different dosages of TBHQ (100, 250, 500, 1000 and 2000 ppm) and were named as WA_1, WA_2, WA_3, WA_4 and WA_5 respectively. Then Rancimat test was conducted to study the oxidation stability of different dosages of TBHQ. The IP recorded for biodiesel with five dosages of TBHQ has been presented in Table 1 and compared with results of ginger extract given in table 2. It is observed that there is an increase in induction period after addition of the antioxidant TBHQ and ginger extract with increasing concentrations.

Table 1: IP recorded for biodiesel with different concentrations of TBHQ (0 days)

Serial number	biodiesel samples doped with TBHQ	Induction Period (IP)
1	$WA_{1(100ppm)}$	6.34 h
2	$WA_{2(250ppm)}$	8.40 h
3	$WA_{3(500ppm)}$	13.43 h
4	$WA_{4(1000ppm)}$	19.22 h
5	$WA_{5(2000ppm)}$	25.12 h

Table 2. IP recorded for biodiesel with different concentrations of ginger extract (0 days)

Serial number	Samples doped with ginger extract	Oxidation stability
1	$BG_{0(0ppm)}$	4.03 h
2	$BGX_{1(100ppm)}$	6.21h
3	$BG_{1(250ppm)}$	8.01 h
4	$BG_{2(500ppm)}$	11.03 h
5	$BG_{3(1000ppm)}$	17.24 h
6	$BG_{4(2000ppm)}$	23.99 h

3.2 Comparison between TBHQ and Ginger Extract after 180 days of storage period

The results demonstrated that a minimum doping of 100 ppm of ginger extract and TBHQ in pongamia biodiesel has met both American (ASTM D-6751) and European (ENE14214) standard specification for biodiesel oxidation stability of minimum IP of 3 h and 6 h and can be used as antioxidant for biodiesel (see table 1 And table 2). The induction periods recorded after 180 days of storage periods has shown that the antioxidant plays a important role in protecting the biodiesel because the BG_0 with no antioxidant has shown a low IP which not acceptable to any specification but the minimum doping of 100 ppm of both the (Ginger extract and TBHQ) antioxidants still satisfies the ASTM standard specification showing an IP of more than 3 h (see table 3 and table 4).

Table 3: IP recorded for biodiesel with different concentrations of TBHQ (180 days)

Serial number	biodiesel samples doped with TBHQ	Induction Period (IP)
1	$WA_{1(100ppm)}$	3.11 h
3	$WA_{2(250ppm)}$	6.30 h
4	$WA_{3(500ppm)}$	7.37 h
5	$WA_{4(1000ppm)}$	10.75 h
6	$WA_{5(2000ppm)}$	13.23 h

Table 4. IP recorded for biodiesel with different concentrations of ginger extract (180 days)

Serial number	Samples doped with ginger extract	Oxidation stability
1	$BG_{0(0ppm)}$	1.03 h
2	$BGX_{1(100ppm)}$	3.01h
3	$BG_{1(250ppm)}$	6.21 h
4	$BG_{2(500ppm)}$	7.02 h
5	$BG_{3(1000ppm)}$	9.24 h
6	$BG_{4(2000ppm)}$	12.99

4. CONCLUSION

The addition of ginger extract can act as antioxidant and it can be recommended as a natural antioxidant for biodiesel, therefore, it can be added as natural additive to biodiesel. The comparative study of antioxidant activity of TBHQ and Ginger extract revealed ginger extract's efficacy in protecting biodiesel and can be taken as an alternative to synthetic antioxidant. The use of ginger extract in place of TBHQ can be equally efficient in protecting biodiesel.

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