



Evaluation of the effectiveness of potato peel extract as a natural antioxidant on biodiesel oxidation stability



Anuchaya Devi^{a,*}, Vijay Kumar Das^b, Dhanapati Deka^a

^a Biomass Conversion Laboratory, Department of Energy, Tezpur University, Napaam, 784028, Assam, India

^b Indiana University, Department of Chemistry, 800 E. Kirkwood Av. Bloomington, IN, 47405, USA

ARTICLE INFO

Keywords:

PPE
Antioxidant
Mesua ferrea L. Biodiesel
Induction period
Rancimat

ABSTRACT

Herein, the potato peels which are the huge household and agro-industrial disposable waste material have been evaluated as a promising and sustainable natural antioxidant for enhancing the oxidation stability of the biodiesel produced from Nahar (*Mesua ferrea* L.) oil. A sample of biodiesel without PPE (Potato peel extract) denoted as BP₀ (0 ppm) and total of four treatments of biodiesel with PPE i.e., 100 ppm (BP₁), 150 ppm (BP₂), 200 ppm (BP₃), 250 ppm (BP₄) were prepared for evaluating the effectiveness of PPE in oxidation stability enhancement. The oxidation stability of all the samples was evaluated with the help of Rancimat instrument manufactured by metrohm. The results revealed that a minimum concentration of 150 ppm of PPE in *Mesua ferrea* L. biodiesel was capable of enhancing its IP (induction period) from 5.63 h to 6.21 h, which met the standard European (ENE14214) biodiesel specification for oxidation stability. Comparison of PPE with TBHQ (*tert*-butylhydroquinone) has also been accomplished to know the effectiveness of PPE against TBHQ. The results in this study have shown that PPE is equally capable of enhancing oxidation stability of *Mesua ferrea* L. biodiesel as compared to TBHQ. Hence, PPE can be used as natural antioxidant for biodiesel instead of using synthetic antioxidant TBHQ procured from non-renewable source.

1. Introduction

The environmentally benign energy resources are always fascinating due to their environmental benefits (Buosi et al., 2016). In this context, biodiesel over petro-diesel should be highlighted because of their renewable and non-toxic nature. But according to reports biodiesel is susceptible to oxidation which may affect its long term storage (Devi et al., 2017 and Sarin et al., 2010). The fuel may get degraded before it can be used and the by-products of biodiesel oxidation are harmful for the engines (Knothe, 2007). Peroxides and hydroperoxides are the main products of oxidation in biodiesel with further degradation; these products form short-chain compounds like acids, aldehydes, ketones and alcohols. The presence of alcohols decreases the flash point and the presence of acids increases the total acidity and the risk of corrosion. Further reactions with the unstable hydroperoxide species with another fatty acid chain may form high molecular weight materials, such dimer or trimer acids which may lead to filter blocking, injector failures and deposit formation (Karavalakis et al., 2010). Oxidation stability of biodiesel is an essential quality criterion for its commercial possibility. In order to commercialize, the oxidation stability of biodiesel produced from various feedstocks should be well understood and meet the

standards. The established European standard for measuring oxidation stability (EN 14112) using a Rancimat instrument is one of the test methods for determining oxidative stability of biodiesel at 110 °C, with a minimum IP of 6 h.

In order to overcome the issues associated with the stability of biodiesel, synthetic antioxidants such as BHA (butylated hydroxyanisole), BHT (butylated hydroxytoluene) and TBHQ are used as additives. However, the use of these synthetic antioxidants are not encouraged because they are derived from petroleum products, which contaminate the renewable nature of biodiesel and also may implicate many health risks, including cancer (Karavalakis et al., 2010). Due to these safety concerns and search for a renewable alternative, there is an increasing trend to replace these synthetic antioxidants with natural ones, which, in general, are supposed to be safer. Phenols are one of the most important groups of natural antioxidants (Artajo et al., 2006). They occur especially in plant material and are known to protect easily oxidizable constituents from oxidation. Polyphenols possess ideal structural chemistry for free radical scavenging activity and they have been shown to be more effective antioxidants in vitro than tocopherols and ascorbate. Antioxidant properties of polyphenols arise from their high reactivity as hydrogen or electron donors and from the ability of

* Corresponding author.

E-mail address: anuchaya.tezu13@gmail.com (A. Devi).

the polyphenol derived radical to stabilise and delocalise the unpaired electron (Rice-Evans et al., 1997).

In this context, phenolic compounds, extracted from potato (*Solanum tuberosum* L.) peel, can be used to prevent oxidation of food containing high amounts of lipid. Phenolics are concentrated in the peel and adhesive tissues, and present in lower amounts in the tuber. Phenolic compounds are present in both free and bound forms. They are mostly substituted derivatives of hydroxycinnamic acid (free form phenolics) and hydroxybenzoic acid (bound form phenolics). The most common hydroxycinnamic acid derivatives in potato peel are CGA (chlorogenic acid), CFA (caffeic acid), and FRA (ferulic acid), while GAC (gallic acid), PCA (protocatechuic acid), VNA (vanillic acid), and PBA (p-hydroxybenzoic acid) are derivatives of hydroxybenzoic acid (Singh and Saldaña, 2011).

Processing of potato products generates a large amount of waste during peeling and trimming causing handling problems. However, a new aspect of concerning the use of these wastes as by-products for further production of additives is gaining interest because these bio-actives are high value products and their use may be economically captivating (Mohdaly et al., 2010). Phenols are found to be present in the potato peels and they are known for their antioxidation potential (Foti, 2008).

In a report, the efficacy of potato peels in vegetable oil protection was demonstrated (Mohdaly et al., 2010). In their study it has been discussed that the potato peels contains significant amount of phenolics and can be comparable to the artificial antioxidants in its efficacy while using in vegetable oil. Thus, with reference to above, the objective of the current work is to test the efficacy of PPE in biodiesel. To the best of our knowledge, the present research is one of the first reports on investigating the oxidation stability enhancement of biodiesel using PPE. Furthermore, it is a step towards waste minimization in terms of converting it into value added product and finding alternative renewable antioxidant in place of synthetic ones.

2. Materials and methods

2.1. Materials

Mesua ferrea L. or locally known as Nahor oil was collected from the locality of Tezpur University campus and the oil has been extracted through solvent extraction method using hexane (Bora et al., 2018). Potato (*Solanum tuberosum* L.) peels were obtained from the kitchen of Pobitora madam curie Women's hostel, Tezpur University, Tezpur, Assam, India. The peels were generated as kitchen waste in the process of daily meal making in hostel. Methanol, ethanol, hexane, H₂SO₄ (Concentrated sulphuric acid, 98%), Na₂SO₄ (anhydrous sodium sulfate), KOH (potassium hydroxide) and phenolphthalein were procured from Sigma Aldrich, Kolkata, India and used as received.

2.2. General instrumental methods

The phenolic compounds present in the prepared PPE were identified by FTIR (Fourier transform infrared spectroscopy) and the spectra recorded as KBr pallets in a Nicolet, USA (Impact 410) FT-IR spectrophotometer, IR regions was used for analyzing the samples; ¹H NMR (Proton Nuclear magnetic resonance) was recorded in a 400 MHz NMR spectrophotometer (JEOL, JNM ECS, Japan) using TMS (tetramethylsilane) as the internal standard; the samples were prepared in CDCl₃. HPLC (High-performance liquid chromatography) Waters Corporation, USA, spectra were performed in UV visible detection-2489, refractive index detector-2414, HPLC pump-515. The mobile phase consisted of 80:20 v/v ethanol: water and the flow rate was 1.0 ml/min. The elution was monitored at 280 nm for 20 min. The sample injection volume was 20 µl. The powder XRD (X-ray diffractograms) of the PPE extract were recorded on a Rigaku miniflex diffractometer (Cu-Kα radiation, λ = 1.5406 Å), Bruker AXS, Germany,

D8 focus, in 2θ range 10–80° at a scanning rate of 2°. The morphological features of the PPE extract were studied by means of SEM (Scanning Electron Microscopy) (Jeol, JSM-6390LV, Japan). The sample was prepared by Pt coating. TEM (Transmission electron microscopy) analysis was carried out in TECNAI G2 20 S-TWIN (200KV); Resolution: 2.4Å, TIA (FEI imaging software), EMMENU4, EMTTOOLS, FEI company, USA. The sample (10 µl) was prepared by dispersing in ethanol on carbon coated Cu grid. Surface pore size analyser was done in NOVA 1000E, NOVA WIN, quantachrome, USA. The sample was prepared by drying in an oven followed by putting in the tube and heated to degas (Devi et al., 2017).

2.3. Procedure for biodiesel production

The crude Nahor oil extracted has been found to contain a high acid value of 15.7 mg KOH/g. This indicates that a two-step transesterification process is required for biodiesel production for effective base catalyzed transesterification. Acid esterification has been done to reduce the acid value of the feedstock. 25 g of Nahor oil was reacted with concentrated H₂SO₄ (1.0% based on the oil weight) as a catalyst and the molar ratio of methanol to oil was 6:1 and the reaction was carried out for 3 h at 60 °C. Reactant samples were collected at regular intervals of 1 h and acid values were calculated. The reaction was continued till the acid value reduced to 1. The esterified oil was then transesterified with the 2 wt% of KOH as base catalyst for 6 h at 70 °C (Boro et al., 2014). The mixture was stirred continuously till the completion of the reaction. Then the reaction mixture was transferred to separating funnel and allowed to settle. The phases were then separated, upper phase was biodiesel and lower phase contained glycerine. Excess methanol was separated from the mixture using rotary vacuum evaporator (EYELA, Clarkson 266459 1 L Rotary Evaporator N-1300V-W 115 V, NJ, USA) at 30 °C and 0.1 MPa. Upper phase i.e. methyl ester (biodiesel) was washed with distilled water for five times to neutralise the catalyst along with the removal of glycerine. Finally biodiesel was dried over Na₂SO₄ (anhydrous sodium sulphate) and physico-chemical properties were checked according to European ENE 14214 standard methods. The percent yield of transesterification has been identified through ¹H NMR where oil conversions (as methyl ester content) were determined by comparing methoxy protons of the methyl ester (~3.6 ppm) and α-methylene protons (~2.3 ppm) as shown in Eq. (1) (Gelbard et al., 1995).

$$C_{\text{MEster}}(\%) = \frac{2 \times A}{3 \times B} \times 100 \quad (1)$$

A = integral of methoxy methyl ester peak at 3.6 ppm

B = integral of α-methylene peak at 2.3 ppm

2.4. Preparation of potato peel extract

Freshly collected peels were washed with distilled water and dried at 45 °C in hot air oven for 72 h and then the dried peels were ground into powdered form. Samples weighing 10 g were transferred carefully into a glass bottle and 100 mL of 100% (v/v) ethanol was added. The glass bottle was gradually shaken (150 rpm) in 25 °C to mix up the materials for 3 h. The supernatant was collected through decantation, centrifuged at 4000 g for 20 min at 25 °C. Ethanol present in the sample was evaporated using rotary evaporator (EYELA, Clarkson 266459 1L Rotary Evaporator N-1300V-W 115 V, NJ, USA) at 30 °C and 0.1 MPa and the extract was stored at 4 °C until use (Farvin et al., 2012).

2.5. Biodiesel preparation for determination of the oxidation stability

Mesua ferrea L. biodiesel free from PPE (BP₀), *Mesua ferrea* L. biodiesel containing 100 ppm of PPE (BP₁), *Mesua ferrea* L. biodiesel containing 150 ppm of PPE (BP₂), *Mesua ferrea* L. biodiesel containing 200 ppm (BP₃) and 250 ppm (BP₄) were prepared for evaluating the

Download English Version:

<https://daneshyari.com/en/article/10117054>

Download Persian Version:

<https://daneshyari.com/article/10117054>

[Daneshyari.com](https://daneshyari.com)