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Full Length Article

Ginger extract as a nature based robust additive and its influence on the oxidation stability of biodiesel synthesized from non-edible oil

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HIGHLIGHTS

- Novel application of ginger extract as an antioxidant to biodiesel.
- *Pongamia pinnata have* been used as a source for biodiesel production.
- Remarkable enhancement in oxidation stability of biodiesel doped with ginger extract.
- Ginger extract could be a potential novel, nature based and renewable biodiesel additive.

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ABSTRACT

Oxidation Stability is one of the most important fuel quality criterions for biodiesel and primarily affects the stability of biodiesel. Therefore, in the present work, antioxidant activity of ginger extract was studied as a method to increase oxidation stability of *Pongamia pinnata* biodiesel. Ginger extract is a nature based renewable substance and has antioxidant property. The presence of phenolic compounds in ginger extract was identified by HPLC, FT-IR and 1H NMR technique. The ginger extract was further characterized by BET, powder XRD, SEM and TEM techniques. The antioxidant activity of different concentrations of ginger extract was tested against radical 2,2-diphynyl-1-picrylhydrazyl (DPPH). A total of five treatments of Pongamia biodiesel doped with ginger extract i.e. 0 ppm (BG_0), 250 ppm (BG_1), 500 ppm (BG_2), 1000 ppm (BG_3), and 2000 ppm (BG_4) were prepared for evaluating the oxidation stability. The oxidation stability of all the samples was evaluated with the professional biodiesel Rancimat instrument manufactured by metrohm. 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. These studies prove to be beneficial in the exploration of natural antioxidant sources for preservation of biodiesel which keeps its renewable nature intact unlike synthetic antioxidants which compromise the renewable nature of biodiesel because most of the synthetic antioxidants are made from petroleum sources.

1. Introduction

Oxidation stability is one of the most important fuel quality criterions for biodiesel [1]. Biodiesels are very susceptible to oxidation processes and consequently oxidation reactions are one of the major sources of quality deterioration. The changes occurring in biodiesel as a result of these oxidation processes make biodiesel completely unsuitable for engine and may stop the engine [2]. Biodiesel has several environmental advantages over petro diesel as it is renewable, non toxic and biodegradable. Biodiesel degrades more rapidly than the later and hence, does not pose a long-term harm to the environment. However, this can also be disadvantageous if the fuel degrades before it can be utilized.

Biodiesel readily undergoes oxidation because of its diverse level of unsaturation in the oil structure; almost all the biodiesels have significant amounts of esters of oleic, linoleic and linolenic acids. The order of decreasing stability is oleic > linoleic > linolenic [3]. The oxidation chain reaction is primarily initiated at the position allylic to double bond. Therefore, fatty acids with methylene-interrupted double bonds, for example, linoleic acid [(9*Z*, 12*Z*)-octadecadienoic acid], are more susceptible to oxidation because of containing methylene groups which are allylic to two double bonds. Fatty acids with two such methylene groups,

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for instance, linolenic acid [(9*Z*, 12*Z*, 15*Z*)-octadecatrienoic acid], are even more susceptible to oxidation. Oxidation process is reported in the literature and relative rates of oxidation are 1 for oleates, 41 for linoleates and 98 for linolenates. Because of these reasons, biodiesel is comparatively unstable when stored. Residual products of biodiesel such as insoluble gums, total acids, and aldehydes formed due to degradation may cause engine problems like filter clogging, injector coking, and corrosion of metal parts and eventually deteriorate the fuel quality. Therefore, oxidation stability is an important quality criterion for biodiesel [4].

The quality of biodiesel is ensured by various standards like EN-14214 and ASTM D-6751 and oxidation stability is among the screened parameter as EN-14214 calls for determining oxidative stability at 110 °C with a minimum IP (induction period) of 6 h by Rancimat method (EN14112) and ASTM standards D-6751 has introduced recently having a minimum IP of 3 h in 2006 by the same method. Indian standard IS-15607 also requires a minimum induction period of 6 h [5]. To meet the specifications, costly synthetic additives are added to the biodiesel but addition of such antioxidants increase production costs while demeaning the renewable nature of the biodiesel because these additives are usually obtained from fossil-based feedstock. Understanding the non-renewable nature of commercial additives, it has become necessary to seek renewable nature based alternative sources of antioxidant compounds for enhancing oxidation stability of biodiesel [6].

Antioxidant functions by scavenging free radicals as soon as they come into existence. The use of antioxidants delays the onset of oxidation until the antioxidant is exhausted and oxidation commences. Therefore, the fatty materials should not be exposed to oxidation-promoting factors as far as possible even when using antioxidants. Most raw vegetable oils contain antioxidants naturally, for instance vitamin E (tocopherols and tocotrienols; four species of each α, β, γ, δ, exist) but the amount of antioxidant in vegetable oils gets reduced in refining process. Other deliberately added synthetic materials such as butylated hydroxytoluene (BHT), butylated hydroxyanisol (BHA), tert-butylhydroquinone (TBHQ) or propyl gallate (PG) [7]. Butylated hydroxyanisol (BHA) is a remarkable synthetic antioxidant on stabilizing oils and fats particularly vegetable polyunsaturated oils, both raw and refined but toxicological studies have shown the possibilities of these antioxidants to present carcinogenic effects in experiments with animals. Due to this fact, the application of synthetic antioxidants is restricted in some countries [8]. Because of the various negative attributes of synthetic antioxidants as aforementioned, it is very essential to explore some natural antioxidants which can provide stability to biodiesel from oxidation and on the other hand remains renewable, non-toxic as well as cost effective. In this context, the ginger extract obtained from fresh ginger root could be an interesting and novel source of antioxidants for biodiesel. This liquid, when obtained from ginger biomass, contains a significant amount of phenolic compounds that have been demonstrated to have a high antioxidant power. This could make its possible use as an additive to enhance the stability of biodiesel against oxidation [9].

Ginger (*Zingiber officinale* Rosc.) originated in SouthEast Asia and belongs to the family Zingiberaceae. The leading ginger producing countries are India, China, Nepal, Nigeria, and Thailand respectively. It is then widely accepted in many countries as a spice and natural additive to add flavour as well as a preservative to food [10]. Besides this application, the rhizome of ginger has also been utilized in traditional herbal medicine. The health promoting perspective of ginger is attributed to its rich photochemistry [11]. Jolad et al. grouped fresh ginger into two wide range categories, i.e. volatiles and non volatiles. Volatiles include sesquiterpene and monoterpenoid hydrocarbons providing the distinct aroma and taste of ginger. On the contrary, non-volatile pungent compounds include gingerols (Fig. 1), shogaols (Fig. 1), paradols, and zingerone [12]. Jorge and Andreo reported ginger extract in soybean oil and measured its antioxidant capacity. They conclude that the ginger extract demonstrates protection activity for soybean oil against lipid oxidation and therefore, it can be used as a natural antioxidant [13].

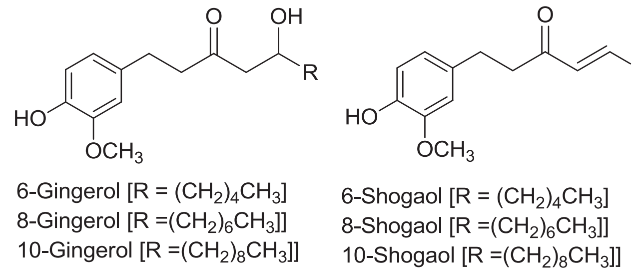

Fig. 1. Chemical structures of the various gingerol and shogaol analogues from ginger rhizome.

Zia-ur-Rehman's group described the application of ginger extract for 6 months of storage of refined sunflower oil at 25 °C and 45 °C and showed good thermal stability, 85.2% inhibition of peroxidation of linoleic acid when heated at 185 °C for 120 min. Therefore, the use of ginger extract in foods is recommended as a natural antioxidant to suppress lipid oxidation [14]. To the best of our knowledge, ginger extract has been used in food industry and tested in soybean as well as sunflower oil in the form of an antioxidant and established as an additive but none of the reports demonstrate the use of ginger extract in biodiesel as an additive for enhancing the oxidation stability. Thus, with this notion in mind, the objective of the present work is to use ginger extract derived from the fresh ginger root in small amount to biodiesel in order to evaluate its potency as a novel, inexpensive, and renewable additive that could be an alternative biodiesel antioxidant for oxidation stability enhancement of biodiesel.

2. Materials and methods

2.1. Biodiesel sample preparation

Pongamia biodiesel was produced from *Pongamia pinnata* oil through transesterification process involving the reaction of oil with methanol under reflux conditions. The experimental 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

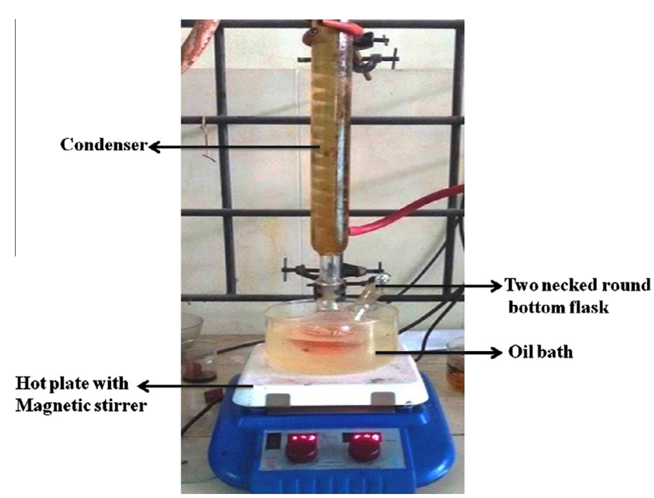

Fig. 2. Schematic representation of the experimental setup.