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Research article

Antioxidants for biodiesel: Additives prepared from extracted fractions of bio-oil

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ABSTRACT

Unlike petroleum diesel, the chemical structure of biodiesel makes it prone to oxidation during long-term storage, thus involving fuel quality deterioration. Therefore, the addition of antioxidants is usually required to meet the quality standards for biodiesel commercialization. Synthetic sterically-hindered phenols have been usually employed for this purpose as free radical scavenging antioxidants. However, naturally occurring phenolics are also available, for example, in the bio-oil produced in the pyrolysis of lignocellulosic biomass. In this work, the antioxidant potential of extracted fractions of lignocellulosic bio-oil has been evaluated. Different organic solvents were tested as extraction agents, acetate esters being the best ones for incorporating bio-oil antioxidant compounds into biodiesel. In the best case, the incorporation of a small concentration of bio-oil compounds (<4 wt.%) led to an improvement of the biodiesel oxidation stability of 475% which, in our case, was enough to meet the European standard requirement.

1. Introduction

The industrial development and growth of any country is inevitably linked to fuel consumption. In this context, diesel fuels have gained an increasingly important role in the heavy transport sector. However, the rapid depletion of crude oil resources and the worldwide awareness about environmental damages have encouraged an increasing interest in alternative renewable fuels. In this context, biodiesel appears as the renewable and clean alternative to petroleum diesel to be used in conventional compression ignitions engines with little or no modification, providing less harmful emissions and enjoying the inherent advantages of being a renewable fuel [1].

Biodiesel is largely composed of a mixture of long chain fatty acid monoalkyl esters (FAME) and can be commercially produced through the transesterification reaction of natural triglycerides with a short chain alcohol. Although the technology for converting edible oils such as sunflower oil, palm oil, soybean oil, coconut oil or rapeseed oil to biodiesel has been well established [2,3], this practice is gaining serious global concern on preserving food security of the planet. Therefore, there is a marked trend towards abolition of the use of edible oils for fuel production, encouraging the use of biofuels derived from non-edible lignocellulosic plants and wastes [4]. In this context, various non-edible crops such as jatropha, jojoba, karanja, castor and algae [5–7], as well as animal fats and waste cooking oils [8–10], have been successfully utilized as feedstock for biodiesel production. This wide variety of raw materials leads to different properties of the final fuel, as these are heavily dependent on the parent oil composition and more specifically on the structure of the fatty acids chains [1,11]. In order to ensure the use of biodiesel in conventional diesel engines without any significant modification, properties of both fuels have to be comparable, which is not always the case [12]. Among these, poor oxidation stability of biodiesel is an important drawback to be considered during long periods of storage of this fuel [13]. The oxidation process causes changes in chemical and physical properties of biodiesel, leading to degradation of the fuel quality because of the formation of oxidation products such as aldehydes, alcohols, carboxylic acids, insoluble gums and sediments that involve fouling problems and shorten engine life [14].

The vulnerability of biodiesel to oxidation is mainly related to the presence of polyunsaturated fatty acids chains in the ester molecules, which easily react with oxygen as soon as being exposed to air. Generally, the rate of oxidation of fatty acids alkyl esters depends on the number of double bonds and their position on the chain: the higher the number of bis-allylic methylene groups in biodiesel, the more prone is to oxidation [13–15]. Saturated compounds have good oxidation stability but, in contrast, they fail in cold temperature properties [8,11].

The oxidation stability is one of the monitored parameters in the biodiesel quality standards (EN 14214 in Europe and ASTM 6751 in USA). Currently, the addition of antioxidants is usually required to fulfill the minimum threshold of oxidative stability established for biodiesel commercialization. Although oxidation cannot be entirely prevented by using antioxidants, it can be significantly retarded. Sterically hindered phenols and secondary aromatic amines are known to be free radical scavenging antioxidants that inhibit oxidation via chain termination

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reactions [15]. These functional groups (OH or NH) contain highly labile hydrogen that can be easily abstracted by the peroxide free radical formed in the initiation and propagation steps of biodiesel oxidation, thus preventing the removal of hydrogen from a carbon of the fatty acid chain [16].

Some works have been published on the effect of the addition of natural and synthetic oxidation inhibitors on biodiesel stability. *Tert*-butyl hydroxyquinone (TBHQ), butylated hydroxytoluene (BHT), 3-*tert*-butyl-4-hydroxyanisole (BHA), pyrogallol (PY) and propylgallate (PG) are among the most studied synthetic antioxidants [17–20]. According to these studies, the antioxidant performance of such additives depends on factors such as the raw material used for biodiesel production or the additive concentration. In general, minimum dosages of 200–1000 ppm of these additives are required to achieve a significant improvement of the oxidation stability of biodiesel. Besides synthetic additives, naturally occurring compounds, such as tocopherols present in edible vegetable oils, have been tested as additives for biodiesel [21–24].

Natural phenolic compounds are not only present in edible oils, but can also be obtained from non-edible plants [25]. In fact, lignin, which is one of the three main building blocks of lignocellulosic biomass together with cellulose and hemicellulose, is the only renewable polyphenolic polymer. Therefore, upon thermal degradation, lignin could be a potential substitute for petroleum-based phenolics. Various thermochemical conversion technologies can be applied for fragmentation and depolymerization of lignocellulose into lower molecular weight molecules, pyrolysis being one of these processes [26,27]. Bio-oil produced by the pyrolysis of lignocellulosic biomass contains over 400 different chemical compounds classified into different categories: organic acids, aldehydes, ketones, furans, sugar based components, and phenolic compounds such as phenol, dimethylphenol, guaiacol, catechol, and syringol [28]. These mono-lignols are formed from the lignin fraction and may account for 6–15 wt.% of the liquids derived from lignocellulosic biomass pyrolysis [29]. These valuable chemicals can be used in a wide range of applications related to the synthesis of pharmaceuticals and food additives and the production of adhesives and resins [28]. On the other hand, the known antioxidant potential of phenols is an interesting factor for exploring new value-added applications of bio-oil. Some works have been published in this field by preparing mix fuels composed of bio-oil (10–50% w/w) and biodiesel [30,31]. The addition of bio-oil to biodiesel resulted in an increase of the oxidation induction temperature from 155 to 225 °C [30], which suggests that some of bio-oil compounds act as antioxidants and protect bio-diesel from degradation. Although most of the tested properties remained within specifications, some fuel properties of the biodiesel rich phase, such as the heating value, water content, density, viscosity or carbon residue deteriorated with respect to those of neat biodiesel [31].

The potential use of bio-oil as an antioxidant for protecting biodiesel from auto-oxidation has been further investigated in this work. As solubility of pyrolysis oil in biodiesel is known to be relatively low [31], different organic solvents were tested as extraction agents during the additive formulation in order to improve both the extraction and the solution of phenolics from bio-oil in biodiesel. The antioxidant performance of the resulting additives was evaluated through their incorporation as small-dosage additives for biodiesel, and not as a mix fuel formulation.

2. Material and methods

2.1. Synthesis of sunflower biodiesel

The biodiesel employed in this study was produced from sunflower oil. Although being edible oil, sunflower oil was chosen as a model raw material for testing the antioxidant additives because of its high degree of unsaturated fatty acids [2].

Sunflower biodiesel was synthesized in our laboratory by catalytic transesterification of refined sunflower oil with methanol as aliphatic alcohol and KOH as alkaline catalyst (oil/alcohol = 1/6 M ratio; mass of catalyst = 1% of oil mass). The mixture was heated with stirring in a batch reactor under reflux at atmospheric pressure and at a temperature of 60 °C for 3 h. Once cooled, the liquid product was poured into a separation funnel and was separated into two phases: biodiesel rich phase and glycerin rich phase. Excess methanol in the biodiesel rich phase was distilled off under vacuum conditions. Then, biodiesel was washed several times with acidulated water to remove the traces of residual glycerin, unreacted catalyst and soap formed during the transesterification process. After that, biodiesel was kept under vacuum in a rotary evaporator to get rid of residual moisture and was further dried with anhydrous magnesium sulfate. Several batches of biodiesel were prepared and kept at −18 °C.

2.2. Preparation of the antioxidant additives and addition to biodiesel

The bio-oil used for preparing the biodiesel antioxidant additives was kindly supplied by the Biomass Technology Group, from Enschede (The Netherlands). This bio-oil was produced during the fast pyrolysis of pinewood. The GC-MS qualitative analysis of its composition (Agilent 7890A/5975C GC-MS) showed the presence of various phenolic compounds (Table 1). Water content was determined by KF titration (Mettler Toledo V20 KF Titrator) with a result close to 33 wt.%.

The experimental procedure for preparing the antioxidant additives from bio-oil is schematized in Fig. 1. A first extraction of bio-oil compounds was carried out using an organic solvent (bio-oil/solvent mass ratio = 1/1; 25 g of each liquid). Ten solvents with different functional groups were tested, including esters, ketones, ethers, alcohols and aromatic hydrocarbons (Table 2). The selection of such solvents was based on different properties thereof as polarity index, water solubility and density, covering a wide range of values in order to evaluate their effect on the extraction rate of bio-oil compounds and subsequent miscibility with biodiesel. The resulting mixture was shaken and decanted in a separation funnel. Then, biodiesel was added to the separation funnel (biodiesel/bio-oil mass ratio = 1/1) and the whole mixture was properly shaken and decanted. Two liquid phases were observed after decantation, the upper one mainly composed of biodiesel. This biodiesel rich phase was recovered and distillated under vacuum conditions (absolute pressure of 0.1 bar) in a rotary evaporator at 60 °C during 1 h in order to remove the solvent content. Then, the mixture of biodiesel and extracted bio-oil compounds was stirred and centrifuged. The insoluble fraction of bio-oil settled to the bottom of the centrifugation glass, while the homogeneous upper phase, composed of biodiesel and soluble bio-oil compounds, was carefully separated, this being the additive to be incorporated to pure biodiesel. Therefore, because of the removal of the insoluble fraction of bio-oil, the prepared additives were totally soluble in biodiesel, being composed of >50 wt.% of biodiesel itself.

Eleven additives were prepared by using the ten organic solvents shown in Table 2, as well as a reference sample prepared by the direct blend of bio-oil and biodiesel with no solvent in the first extraction stage. Neat biodiesel was doped with the prepared additives at several loadings: 1, 1.8, 3 and 8 wt.%. The oxidation stability of these doped samples was determined just after their preparation. At the same time,

Table 1
Phenolic compounds identified in the bio-oil.

Phenolic compounds
2-methoxyphenol (guaiacol)
4-methylguaiacol
4-ethylguaiacol
4-vinylguaiacol
4-propylguaiacol
5-allylguaiacol
4-propenylguaiacol
vanillin
4-acetylguaiacol
levoglucosan