



Research article

Obtaining biodiesel antioxidant additives by hydrothermal treatment of lignocellulosic bio-oil



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ABSTRACT

The potential use of bio-oil as a small-dosage additive for improving biodiesel oxidation stability has been investigated in this work. Lignocellulosic bio-oil was high-pressure processed under different mixtures of water and organic solvents in order to promote depolymerization of the high molecular lignin still present in bio-oil and increase the content of phenolics, whose antioxidant potential is known. In fact, the antioxidant potential of bio-oil was found to noticeably enhance after the hydrothermal treatment. While the addition of 2% of crude bio-oil improved biodiesel oxidation stability by 135%, the same amount of hydrothermal treated bio-oil (water, 300 °C, 8.5 MPa) led to an oxidation stability improvement of 400%, which was related to the increase in the concentration of catechol, as well as to the modification of antioxidant properties of the pyrolytic lignin fraction.

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1. Introduction

Up to now, fossil fuels such as coal, fuel oil and natural gas have played a prominent role in the energy sector. However, limited resources of these fuels and environmental problems related to greenhouse gas emissions pose the need to develop and promote the use of renewable and clean energy resources that can substitute current fossil fuels.

Biodiesel and bio-oil are just two examples among those renewable resources. Chemically, biodiesel is composed of a mixture of fatty acid methyl esters (FAME) obtained from the transesterification reaction of vegetable oils, waste cooking oil or animal fats with alcohol (methanol or ethanol) in the presence of a catalyst. Biodiesel can be used as an alternative diesel fuel for compression ignition engines, providing less harmful emissions and enjoying the inherent advantages of being a renewable fuel [1]. However, biodiesel commercialization is subject to quality parameters designated by several standards like EN 14214 [2] in Europe or ASTM D6751 [3] in USA. Oxidation stability is among the monitored parameters in these biodiesel quality standards. Generally, factors such as elevated temperatures or the presence of air, light or extraneous materials such as metals or initiators facilitate biodiesel oxidation [4]. Moreover, biodiesel instability is also strongly related to FAME composition and, more specifically, to the number of double bonds and their position on the fatty acid chain, since the oxidation chain reaction is usually initiated at the allylic position to double bonds [4–6]. Therefore, due to the significant presence of polyunsaturated fatty acids chains in biodiesel, poor oxidative stability is one of the major issues

to deal with before supplying biodiesel as a fuel for diesel engines. After long periods of storage, biodiesel degrades as a consequence of air contact and other pro-oxidizing conditions, leading to the formation of low-molecular organic acids or high-molecular polymerization species, among others, that may impair fuel quality and, subsequently, engine performance [6].

Biodiesel degradation mechanism is known to occur through a series of chain reactions that involve the formation of free radicals (peroxyl radical) [7]. Antioxidants such as phenols and amines either have a hydrogen atom that can be “donated” to interrupt the chain reaction and retard biodiesel degradation. The highly reactive hydrogen present in these compounds (OH or NH groups) gets easily abstracted by the peroxy radical rather than any hydrogen in the fatty chain, thus preventing the chain reaction propagation. Usually, biodiesel antioxidants are deliberately-added synthetic phenols such as pyrogallol (PY), *tert*-butyl-hydroquinone (TBHQ), butylated hydroxytoluene (BHT) or butylated hydroxyanisole (BHA) [8–13]. Such compounds are generally added at levels of around 500–1000 ppm, showing different effectiveness results depending on a wide variety of factors, including the fatty acid profile of the raw material and the storage conditions. Naturally occurring antioxidants, such as vitamin E (tocopherols and tocotrienols), are originally present in unrefined vegetable oils, but its concentration and effectiveness are usually damaged after the refining process [4]. The deliberate addition of natural antioxidants to biodiesel, such as α -tocopherol or β -carotene, has also led to good results [12–14], but the edible origin of such compounds could give rise to some controversy. Therefore, the search for antioxidant additives coming from renewable non-food resources appears as an interesting option for improving biodiesel oxidation stability in a sustainable way. In this

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field, hydrothermal processing of olive tree pruning has been reported to produce a phenolic rich liquor showing antioxidant activity [15]. In other work, Kang et al. [16] proved the antioxidant effect of lignin by adding it during the production of biodiesel in supercritical methanol.

Upon thermal degradation, lignocellulosic biomass is a renewable source of high added-value products, including phenols. Among thermochemical processes, pyrolysis of lignocellulosic biomass yields phenolic compounds via the cleavage of ether groups and carbon-carbon linkages from the monolignols building blocks of lignin (coniferyl alcohol, sinapyl alcohol and *p*-coumaryl alcohol) [17]. Phenolic monomers derived from lignin such as phenol, dimethylphenol, guaiacol, catechol, syringol, etc. (GC-detectable compounds) are usually present in bio-oil in a range of 6–15 wt%, while oligomeric structures (non-volatile HPLC-detectable compounds with molecular weights from several hundred to >5000) may account for 15 wt% [18]. Moreover, bio-oil usually contains around 25 wt% of high molecular lignin barely depolymerized during the pyrolysis process [18].

Direct use of bio-oil as an alternative to petroleum fuels is restricted by issues such as its high oxygen fraction, high water content, high viscosity, pH or corrosiveness [19]. In this field, different upgrading treatments such as HDO (hydrodeoxygenation), catalytic cracking or steam reforming can be applied in order to modify chemical composition and physical properties of bio-oil [20]. Although intensive efforts to upgrade bio-oils have resulted in considerable progress, there are still several technical barriers to overcome. Meanwhile, the use of bio-oil as a fuel is not the only approach to be considered, as bio-oils are an interesting source of valuable chemicals [21], such is the case of antioxidants compounds. In fact, biodiesel has been proved to be protected from auto-oxidation and degradation when being mixed with bio-oil at dosages of 10–50% [22–23]. García et al. [24] prepared additives from pine wood bio-oil by a liquid-liquid extraction process using organic solvents and biodiesel itself as sequential extracting agents. Biodiesel oxidation stability was found to improve up to 475% when incorporating 8 wt% of such type of additive prepared with isopropyl acetate as extracting agent [24].

In order to continue this research line, the present work aims at improving the antioxidant properties of bio-oil by increasing its phenolics content through depolymerization of the high molecular lignin still present in bio-oil. Several works in the literature have pointed to the hydrothermal liquefaction of lignin as a promising method for obtaining phenolics [25–27], which have shown antioxidant abilities [16,28].

2. Experimental

2.1. Production of biodiesel

Because of its high unsaturation degree, which makes it very prone to oxidation [29], sunflower biodiesel was employed in this work for

testing the antioxidant potential of the bio-oil based additives. Sunflower biodiesel was synthesized in our laboratory by catalytic transesterification of sunflower refined oil using methanol (>99.8% purity, PANREAC) as aliphatic alcohol (1:6 oil-alcohol molar ratio) and KOH (85% purity, Carbo Erba reagents) as alkaline catalyst (1 wt% of the mass of oil). Biodiesel production process is schematized in Fig. 1 and described in more detail elsewhere [24]. Several batches of biodiesel were prepared, mixed and kept at $-18\text{ }^{\circ}\text{C}$ until further use.

2.2. Production of the antioxidant additives

The antioxidant additives were produced by further processing bio-oil at high pressures and moderate temperatures under different reaction mediums. The obtained products were subsequently added to biodiesel as small-dosage additives (<2%), as detailed below.

2.2.1. Raw material

Bio-oil derived from pinewood pyrolysis was kindly supplied by the Biomass Technology Group, from Enschede (The Netherlands). Several phenolic compounds such as catechol, guaiacol and guaiacol alkylated derivatives (4-methylguaiacol, 4-ethylguaiacol, 4-vinylguaiacol, etc. ...) were identified in the bio-oil by GC-MS analysis (Agilent 7890A GC system combined with Agilent 5975C inert MSD). The water content was measured with a Mettler Toledo V20 KF Titrator and was found to be around 33 wt%.

2.2.2. Bio-oil hydrothermal treatment

The bio-oil hydrothermal treatment was performed in a 125 mL autoclave batch reactor (High Pressure Equipment Company, series GC1), made of stainless steel and designed for pressures up to 82 MPa and maximum temperatures of 425 °C.

In a typical experiment, bio-oil (4 g) and the reaction medium solvent (40 g) were loaded into the reactor, which was properly closed and placed in an electrical furnace. During the experiments, the mixture inside the reactor was continuously stirred with a magnetic drive agitator. Different mixtures of water and organic solvents (4:1 water-organic solvent molar ratio) were used as reaction medium: (i) only water; (ii) water and 1-butanol; (iii) water and ethyl acetate; (iv) water and isopropyl acetate. The use of different solvents provided different functional groups available for reacting with bio-oil, as well as different reaction pressures. Two different reaction temperatures were tested in the experiments, 250 and 300 °C, which led to a reaction pressure in the range of 4–11.5 MPa, mainly corresponding to the vapor pressure of the solvent mixtures. Temperature was limited to 290 °C when working with isopropyl acetate since vapor pressure at 300 °C was very close to the limit of the pressure relief valve connected to the reactor. The operating conditions in the experiments are summarized in Table 1. As can be seen, two of the experiments were replicated in order to evaluate

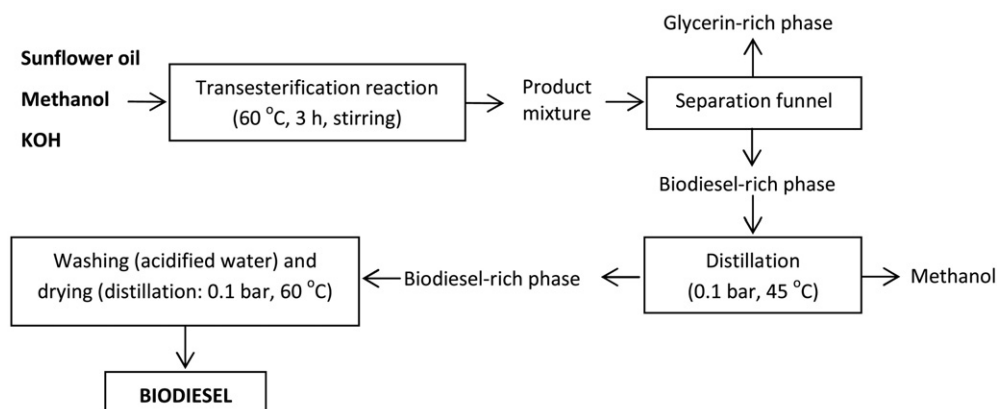


Fig. 1. Biodiesel production process from sunflower oil.

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