HYDROTHERMAL TREATMENT OF BIO-OIL FOR THE PRODUCTION OF BIODIESEL ANTIOXIDANTS

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1.   INTRODUCTION

Fuel consumption is inevitable for industrial development and growth of any country. In the last years, diesel fuels have gained an increasingly important role in the transportation sector. However, the rapid depletion of crude oil resources, as well as the worldwide concern about the environmental damage related to the increase in the emissions of carbon dioxide and other pollutants, has led to an increasing awareness about the development and use of renewable fuels. In this context, biodiesel appears as a good alternative to fossil diesel because of its renewable and biodegradable character, also being a non-toxic and clean fuel that can be used in compression ignitions engines with little or no modification [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 ligno-cellulosic plants and wastes [4].

In spite of its environmental friendly properties, biodiesel commercialization has been limited either by economic issues, related to the high cost of the plant oils, or by technical concerns [3, 5]. In order to ensure the use of biodiesel in conventional diesel engines without any significant modification, the properties of both fuels have to be comparable, which is not always the case. Some properties of biodiesel have to be improved to make it usable in neat form, such as reduction of NOx emission and improvement in cold temperature properties [6]. The poor oxidation stability of biodiesel is another important limitation to be considered during extended periods of storage [7]. The oxidation process causes the degradation of the fuel quality by forming oxidation products such as aldehydes, alcohols, carboxylic acids, insoluble gums and sediments that involve plugging and fouling problems and reduce the engine life [8]. The oxidation stability is one of the monitored parameters in the quality standards for biodiesel commercialization (EN 14214 in Europe and ASTM 6751 in United States) and the addition of antioxidants is usually required to retard oxidation and satisfy the quality standards for biodiesel commercialization. Sterically hindered phenols and secondary aromatic amines are known to be free radical scavenging antioxidants that inhibit the oxidation via chain termination reactions [9]. 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 [10-13].

In addition to synthetic additives, naturally occurring compounds, such as lignin, can be regarded as a rich source of phenols. Various thermochemical conversion technologies, including pyrolysis, can be applied for fragmentation and depolymerization of lignocellulose into lower molecular weight liquid product [14, 15]. Bio-oils produced by the pyrolysis of lignocellulosic biomass contain 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 [16]. These phenolic compounds

are formed from the lignin fraction and may account for 6-15 wt. % of the liquids derived from lignocellulosic biomass pyrolysis [17]. The extraction of part of those phenolic compounds, and his utilization as additive to improve the oxidation stability of biodiesel has been tested with very good results.

However, as a result of the incomplete fragmentation of lignin during pyrolysis, bio-oil can contain up to 30 wt. % of high molecular weight compounds, non-detectable by GC-MS, which can also be a source of smaller phenolic units. This issue has motivated the present work, in which the hydrothermal treatment of bio-oil at high pressure and under different reaction media has been studied, aiming at promoting the depolymerization of the lignin remaining fraction in order to obtain an antioxidant additive for biodiesel, richer in phenolic compounds.

2.   MATERIALS AND METHODS

2.1   Bio-oil

Bio-oil derived from pinewood pyrolysis was used as source of phenolic compounds for the preparation of the antioxidant additives. This bio-oil was supplied by the Biomass Technology Group, from Enschede (The Netherlands). The composition of this bio-oil was qualitatively analyzed by GC-MS (Agilent 5975C Series GC/MSD, HP-5 capillary column). The main phenolic compounds identified in this liquid are listed in Table 1. The water content, determined with a Mettler Toledo V20 KF Titrator, was 32.6 wt. %.

Table 1. Phenolic compounds identified in the bio-oil by GC-MS.

Retention time (min)	Compound
12.70	2-hydroxy-3-methyl-2-cyclopenten-1-one
14.52	2-methoxyphenol
18.28	2-methoxy-4-methylphenol
19.08	1,2-benzenediol
21.47	4-ethyl-2-methoxyphenol
22.98	4-methyl-1,2-benzenediol
23.35	hydroxymethylfurfural
23.94	4-vinylguaiacol
24.75	2-methoxy-4-propylphenol
25.09	2-methoxy-3-(methoxymethyl)phenol
27.33	2,6-dimethylphenol
29.52	isoeugenol
30.29	vanillin
30.63	4-methoxy-3(methoxymethyl)phenol
32.44	2-methoxy-4-propylphenol
33.73	4-acetoguaiacol
35.44	guaiacyl acetone
37.58	4-(3-hydroxy-1-propyl)-1,2-methoxyphenol
44.94	3-(4-hydroxy-3-methoxyphenyl)-2-propen-1-one

2.2   Experimental setup for bio-oil hydrothermal treatment

The hydrothermal treatment of bio-oil was carried out in an autoclave batch reactor. The reactor (series GC1 from High Pressure Equipment Company) was made of stainless steel 316, with a volume of 125 mL and designed for pressures up to 82 MPa and a temperature of 700 K.

In a typical experiment, bio-oil (4 g) derived from the pyrolysis of pinewood was added into the reactor together with the reaction medium composed of water or different mixtures of water and organic liquids (1-butanol, ethyl acetate and isopropyl acetate) at a 4:1 molar ratio (water/organic). The mass ratio between the solvent medium and the bio-oil was fixed at 10:1.

The reactor was supported on a magnetic stirrer plate and a magnet was used to stir the mixture of solvent and

bio-oil during the experiments. The reactor was heated with an electrical furnace and a controller connected to a K-type thermocouple was used to maintain temperature at 250 or 300 ⁰C inside the autoclave. Figure 1 shows a scheme of the experimental setup.
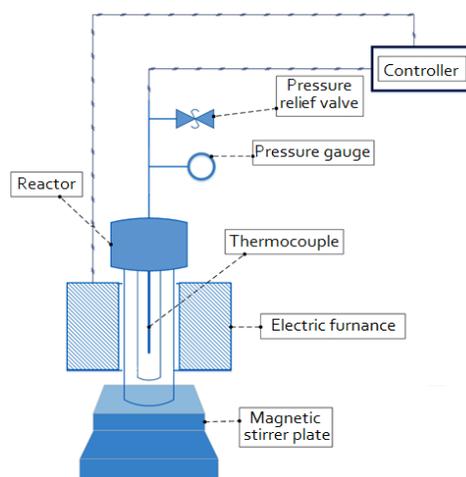

Figure 1. Experimental setup for the hydrothermal treatment of bio-oil.

The operating conditions tested in the hydrothermal experiments are summarized in Table 2.

Table 2. Operating conditions in the bio-oil hydrothermal experiments.

Temperature (⁰C)	Maximum pressure (bar g)	Solvent medium
300	87	Water
250	40	Water
300	108	Water / butanol
250	53	Water / butanol
300	102	Water / ethyl acetate
250	50	Water / ethyl acetate
290	115	Water / isopropyl acetate
250	52	Water / isopropyl acetate

The hydrothermal reaction was kept during 3 h and then, the electrical furnace was turned off and the autoclave was cooled down to room temperature. Once cooled, the liquid product was recovered from the reactor and centrifuged to remove the solid particles formed during the reaction. Then, the solvent medium was removed by distillation in a rotatory evaporator (75 min at 65 ⁰C and 0.1 bar a). The non-distilled liquid was considered as the additive for biodiesel.

2.3   Biodiesel

2.3.1   Biodiesel production

Biodiesel used in this work was produced in our laboratory by transesterification of refined sunflower oil (acidity < 0.5 %) with methanol (> 99.8 % purity, PANREAC) and KOH as alkaline catalyst (85 % purity, Carbo Erba reagents).

The transesterification process took place at atmospheric pressure and 60 ºC in a batch reactor (1000 mL glass vessel) equipped with a mechanical stirrer, a condenser and a heating jacket. Sunflower-oil was added to the reactor and started to be heated. Before reaching the desired temperature, the solution of methanol and catalyst (KOH) was added to the oil with stirring. Excess methanol was used (methanol / oil molar ratio of 6:1) in order to

shift the transesterification reaction to biodiesel (FAME) formation. The amount of catalyst added was 1 wt. % of the oil mass.

The reaction was kept for 3 h to ensure the complete conversion of the oil. Once the liquid mixture was cooled down to room temperature, it was transferred to a separation funnel where the main products, biodiesel and glycerin, were separated into two non-miscible phases. The biodiesel-rich phase was recovered and excess methanol was removed by distillation in a vacuum rotary evaporator. After that, biodiesel was washed with hot distillated water (50 ºC) acidified with some drops of H_2SO_4 to remove the traces of residual glycerin, catalyst and soap formed during the transesterification process. Four washes were required to purify the biodiesel. After that, biodiesel was kept under vacuum in a rotary evaporator (60 ºC and 0.1 bar during 90 min) to get rid of residual moisture. Water content in the final biodiesel was measured by Karl Fischer titration (Mettler Toledo C20 Coulometric KF Titrator) to check that water had been totally removed.

After its production, biodiesel was stored in a high density polyethylene container at 248 K to prevent it from being oxidized before adding bio-oil derived additives.

2.3.2 Doped biodiesel preparation

In compliance with the European Standard EN 14214, content of FAME in commercial biodiesel has to be at least 96.5 wt. %, which leaves a maximum margin of 3.5 % for the presence of impurities and/or the incorporation of additives. In this work, different samples of doped biodiesel were prepared by adding the liquid products resulting from the hydrothermal experiments (once the solvent had been removed on a rotary evaporator) to the prepared biodiesel in a concentration of 2%. The mixture was shaken for 30 min on a magnetic stirrer plate and, then, was centrifuged during 30 min. After centrifugation, it could be observed that the blend was not homogeneous, but the additive was not entirely soluble in biodiesel, meaning that the actual percentage of additive incorporated to biodiesel was below the 2% initially set.

2.3.3 Biodiesel characterization

Both, the neat biodiesel and the doped samples, were characterized according to different techniques, including not only the oxidation stability, but also other important properties such as viscosity and cold filter plugging point.

The oxidation stability (OXY) was measured using the PetroOXY equipment (Petrotest Instruments® GmbH & Co. KG) according to the procedure detailed in the European Standard EN 16091 and in the American Standard ASTM D7545. The breaking point in this type of measurement occurs when the pressure in the sample vessel drops 10 % below the maximum pressure achieved in the test as a consequence of the oxygen consumption. The test result is the required time for such pressure drop, so the greater the measured time, the better the oxidation stability of the biodiesel sample. The oxidation stability improvement of the doped biodiesel samples with respect to the neat biodiesel was calculated according to equation 1.

$$\text{OXY improvement (\%)} = \frac{\text{OXY}_{\text{doped biodiesel}} - \text{OXY}_{\text{neat biodiesel}}}{\text{OXY}_{\text{neat biodiesel}}} \cdot 100 \qquad \text{(equation 1)}$$

The kinematic viscosity of biodiesel was measured at 40 ºC with a capillary glass tube viscometer (Cannon-Fenske viscometer, model 150 T-845) according to the standard ISO 3104:1994.

The cold filter plugging point (CFPP) is the lowest temperature at which a given volume of diesel type of fuel still passes through a standardized filtration device in a specified time when cooled under certain conditions. This test gives an estimate for the lowest temperature that biodiesel will give trouble free flow in certain fuel systems. The equipment used to determine the CFPP was an automated instrument ISL FPP 5Gs (model V22101).

3.   RESULTS

The results of the oxidation stability, viscosity and CFPP of all the doped biodiesel samples are presented in Table 3.

Table 3. Characterization results of the doped biodiesel samples.

Operational conditions during bio-oil hydrothermal treatment for the additive preparation		OXY (min)	Viscosity (cSt)	CFPP (ºC)
Solvent medium	Temperature (ºC)			
Water	300	51.0 ± 0.5	4.23	-5.1
Water	250	33.3 ± 0.3	4.21	-6.2
Water / butanol *	300	39.2 ± 0.4	4.23	-4.0
Water / butanol *	250	35.6 ± 0.2	4.11	-3.9
Water / ethyl acetate	300	25.98 ± 0.02	4.25	-2.9
Water / ethyl acetate	250	17.66 ± 0.01	4.14	-2.9
Water / isopropyl acetate	290	13.71 ± 0.05	4.22	-1.8
Water / isopropyl acetate	250	19.72 ± 0.09	4.14	-4.0

* Results corresponding to the additive derived from the aqueous-rich phase, since after the liquid product centrifugation, the liquid was separated into two phase due to the low miscibility of water and butanol.

The viscosity of the neat biodiesel was 4.20 cSt, so substantial changes of this property were not observed after incorporating the additives. The viscosity of all the doped samples was in compliance with the limits set by the standard EN 14214 (3.5 - 5 cSt). On the other hand, CFPP of the neat biodiesel was -7.3 ºC. The standard EN 14214 sets different limits for this property depending on the climate where biodiesel is going to be used, differentiating between arctic and temperate climates. Even though CFPP was negatively affected by the presence of the additives (filter plugging started at higher temperatures), all the doped biodiesel samples would be suitable to be used in warm climates, for which the CPFF minimum threshold is set at 5 ºC (grade A) and 0 ºC (grade B).

The oxidation stability of the neat biodiesel used for preparing the doped samples ranged between 9.3 and 10.1 min, so a clear improvement of this property was achieved by incorporating certain additives. As can be seen in Figure 2, the additive resulting from the hydrothermal treatment with only water as reaction medium at 300 ºC led to the best result, with an oxidation stability improvement higher than 400 % with respect to the neat biodiesel.
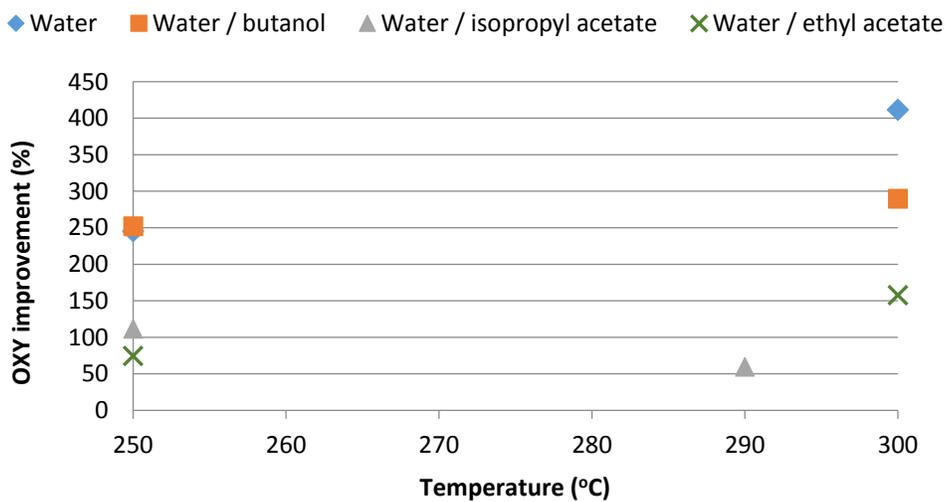

Figure 2. Improvement of the biodiesel oxidation stability as a function of the operational conditions applied for preparing the additives (temperature and reaction medium during bio-oil hydrothermal treatment).

Despite of adding different organic liquids to the hydrothermal treatment of bio-oil with the aim of promoting the reaction and fragmentation of the lignin fraction, results from Figure 2 shows that the use of these organic liquids did not enhance the antioxidant nature of the additive. The best results were obtained when using only water as the reaction medium. Among the different organic solvents used, the use of butanol, which can be considered a hydrogen-donor solvent, led to considerable better results than both isopropyl acetate and ethyl acetate. Regarding the effect of the reaction temperature, the increase from 250 to 300 ºC (linked to an increase in the pressure inside the reactor) was favorable in most cases, except when using the mixture of water and isopropyl acetate. The critical point of the isopropyl acetate is around 300 ºC, so the fact of working at a temperature close to that value seems to damage the antioxidant nature of the product.

The use of the additives produced in the bio-oil hydrothermal treatment was also compared to the direct use of bio-oil as an additive for biodiesel. Biodiesel and bio-oil (2 wt. %) were blended and centrifuged just as it was done with the other additives. The oxidation stability of the resulting biodiesel was 22.5 min, which means an oxidation stability improvement of 135 %. Therefore, the hydrothermal treatment seems an interesting process to improve the antioxidant nature of bio-oil, probably linked to the promoting of lignin fragmentation.

The doped biodiesel samples were qualitatively analyzed by GC-MS in order to identify the incorporated compounds. Phenolic compounds such as 2-methoxyphenol, 2-methoxy-4-methylphenol, 4-ethyl-2-methoxyphenol and 2-methoxy-4-propylphenol were identified in all the samples. However, it was found that biodiesel prepared with the additives obtained in the hydrothermal experiments conducted with only water as reaction medium contained extra phenolic compounds that were only present in such samples: catechol (1,2-benzenediol) and 2,6-dimethoxyphenol. Therefore, the greatest antioxidant power of these additives could be attributed to the presence of such compounds. More efforts are required in this field in order to get a better characterization of the additives and the quantification of the incorporated compounds to biodiesel.

4.   CONCLUSIONS

Hydrothermal treatment of bio-oil appears as an interesting process to promote the depolymerization of the remaining fraction of lignin in the liquid, thus obtaining a product rich in phenolic compounds, whose antioxidant nature is well-known. In this work, hydrothermal treatment of bio-oil was conducted under different operating conditions in order to obtain antioxidant additives for biodiesel. The oxidation stability of biodiesel was considerably improved by incorporating these type of addives at low concentrations (< 2 wt. %), with an improvement higher than 400 % with respect to the neat biodiesel oxidation stability in the best case (with the additive obtained in the hydrothermal treatment of bio-oil with only water at 300 ºC as reaction medium). Other important properties of biodiesel such as the viscosity and the cold filter plugging point were not too affected by the incorporation of the additives. A first qualitative study proved the presence of phenolic compounds in the doped biodiesel, but more work is required in this field to delve into the quantification of these compounds.

5.   ACKNOWLEDGMENTS

6.   REFERENCES

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