The influence of AC and Ni/AC catalyst in the antioxidant additives production from argan shells lignin

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Abstract

In this work, the production of antioxidant additives via hydrothermal treatment of lignin from argan nutshells (agricultural waste) was evaluated. Specifically, the effect of using a catalyst supported on activated carbon which had been prepared from the same waste (argan nutshells) has been studied.

Introduction

Lignin conversion could be considered a potential alternative to the petrochemical industry, especially for fuel and chemicals production [1]. For its chemical valorization, lignin fragmentation can be implemented via various technologies as biological depolymerization, homogeneous and heterogeneous catalysis and thermochemical treatments [2]. Several studies of lignin depolymerization have demonstrated that hydrothermal processes could be a potential way to produce monomers, dimers and oligomers containing phenolic groups, this being a promising and sustainable way to produce additives with potential antioxidant activity.

Biodiesel is essentially composed of fatty acid monoalkyl esters (FAME), which are synthesized through the transesterification of triglycerides with a simple alcohol [3]. Biodiesel tends to be less resistant to oxidative degradation than fossil diesel due to the instability caused by the unsaturation of fatty acid chains [4]. The main role of the antioxidant additives is to prevent the formation of peroxyl radicals by substituting them by new and less reactive radicals (as phenolic radicals) in order to stop the chain degradation. Phenolic compounds have previously been shown to be effective sustainable antioxidants for biodiesel [5].

In a previous work, the lignin-rich fraction obtained from the semi-chemical soda pulping of argan nutshells (AS), an agricultural waste rich in lignin, has been tested for depolymerization and production of antioxidant additives for biodiesel in H_2, CO_2 and HCOOH reaction mediums [6], leading to a significant improvement of the oxidation stability (an improvement of up to 400 %).

The scope of this work reports on studying the effect of introducing either activated carbon (AC) or nickel catalyst supported on activated carbon (Ni/AC) on the yield and characteristics of the antioxidant additive. The activated carbon involved in the preparation of the catalyst was produced by pyrolysis (at 450 °C) of the argan nutshells and subsequent activation with CO_2 (at 900 °C). This involves another valorization route to be explored for this waste.

Materials and methods

Depolymerization of argan nutshells lignin (ASL), dissolved in water at a concentration of 7 wt.%, took place under hydrothermal conditions (300 °C and autogenous pressure for 1 h) in a 500 mL stainless steel stirred reactor. The process was firstly carried out without catalyst and, then, the effect of adding AC or Ni/AC at a mass ratio of 1:1 catalyst:lignin) was evaluated. Ni/AC catalyst was also tested under H_2 atmosphere, by initially loading to the reactor 25 bar H_2 before heating. Table 1 resumes the operational conditions in the experiments.

After the experiment, the aqueous liquid product was recovered from the reactor and filtered. An additional weighted amount of water was used to wash the filtered solid and the reactor walls. Then, the filtered solid was extracted with methanol in a soxhlet extractor (for 36 h). The filtered liquid was extracted using twice the weight of isopropyl acetate. The organic phase extracted (OP) was separated and the solvent was removed in a rotary evaporator at 60 °C and under vacuum conditions. The remaining dried solid, organic phaseadditive OP_{add} from now on, was weighed for quantification purposes and stored. An aliquot of OP obtained in each experiment was analyzed by GC-MS.

On the other hand, the organic fraction extracted with methanol from the filtered solid (SM_{add}) was also quantified and tested as an antioxidant additive. Lately, neat biodiesel prepared from sunflower oil [7]

was doped with 1 wt.% of the dried additives. In order to improve the dissolution of the additives in the biodiesel, methanol was used as a co-solvent (with mass ratio methanol: biodiesel of 1:1), and the mixture was sonicated. Then, methanol was removed in a rotary evaporator. The remaining biodiesel was centrifuged in order to separate the insoluble fraction of the additive. Biodiesel oxidation stability, both before and after the mixing, was measured according to EN 16091 and ASTM D7545 methods utilizing a PetroOXY device.

Results and discussion

- Products yields

During depolymerization, ASL has been mainly converted to water-soluble and water-insoluble solid compounds. Figure 1 shows the yields of both products, calculated over the initial amount of ASL fed. Only a minimal amount of gases was generated in the process. As seen, no differences in the product distribution were observed when loading AC or Ni/AC (with or without the initial pressure of H_2) after the hydrothermal treatment. On the other hand, both extracted additives (OP_{add} and SM_{add}) were affected differently by the operational conditions, as shown in Figure 2. The yield of OP_{add} was enhanced by the presence of the catalyst, obtaining the highest value of 7 wt.% (calculated over the content of organic matter in ASL, which was around XX%) when Ni/AC was introduced to the reaction medium. An inverse trend was observed for the SM_{add}; its yield decreased in the presence of either AC or Ni/AC, which could points to the retention of some organic compounds on the AC even after the long process of the soxhlet extraction or to a different solid nature less extractible with methanol.

- Oxidation tests

Figure 3 resumes the results of the oxidation time of the neat and dopped biodiesel with both OP_{add} and SM_{add} additives. Doping biodiesel with OP_{add} additives clearly improved the oxidation time (14.4 min for the neat biodiesel vs up to 60 min for the biodiesel dopped with OP_{add}), although any significant effect of using catalyst or H_2 atmosphere was found. On the other hand, loading biodiesel with SM_{add} did not show any improvement in the oxidation time when using AC or Ni/AC in the hydrothermal process, while this extractive seemed to have some antioxidant power when the process was carried out without catalyst.

Conclusions

In summary, the main conclusion obtained in this work is that it is possible to produce effective additives from the depolymerization of lignin extracted from argan nutshells, which could be useful for improving the oxidation stability of biofuels. Adding activated carbon (with or without Ni loading) into the reaction medium increased the production of additive, but no significant differences on its antioxidant potential were found when being blended with biodiesel at a small dosage. Further experimental work involving other factors, such as the treatment temperature or the reaction time, is required.

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Figures/ Table

Table 1: Operational conditions in the experiments of ASL depolymerization.

Exp.#	Temperature (°C) / time (h)	Conditions
1 & 2	300 / 1	Without catalyst
3 & 4	300 / 1	AC:lignin (1:1)
5	300 / 1	Ni/AC:lignin (1:1)
6	300 / 1	Ni/AC:lignin (1:1), 25 bar H_2

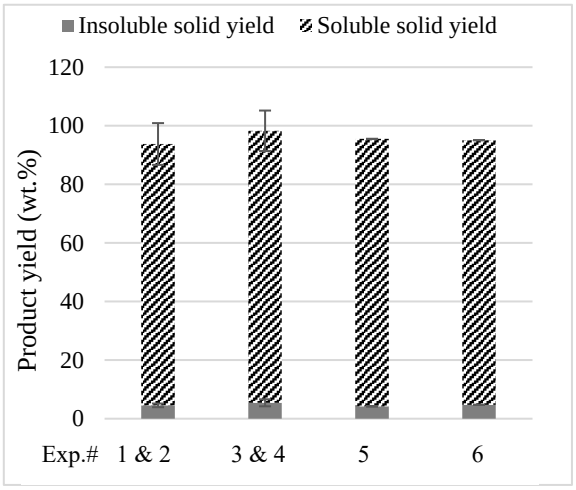

Figure 1: Products distribution.

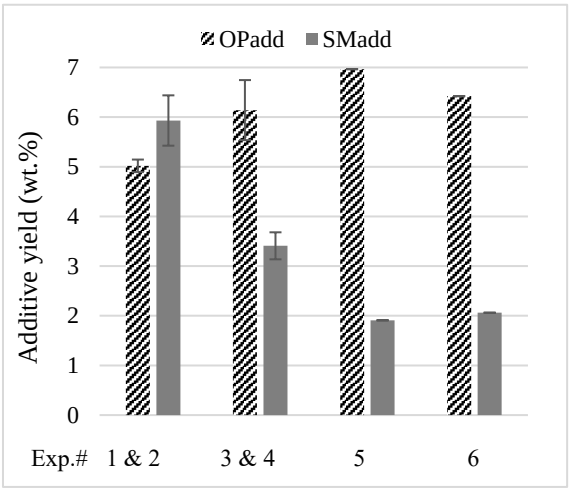

Figure 2: Additive yields.

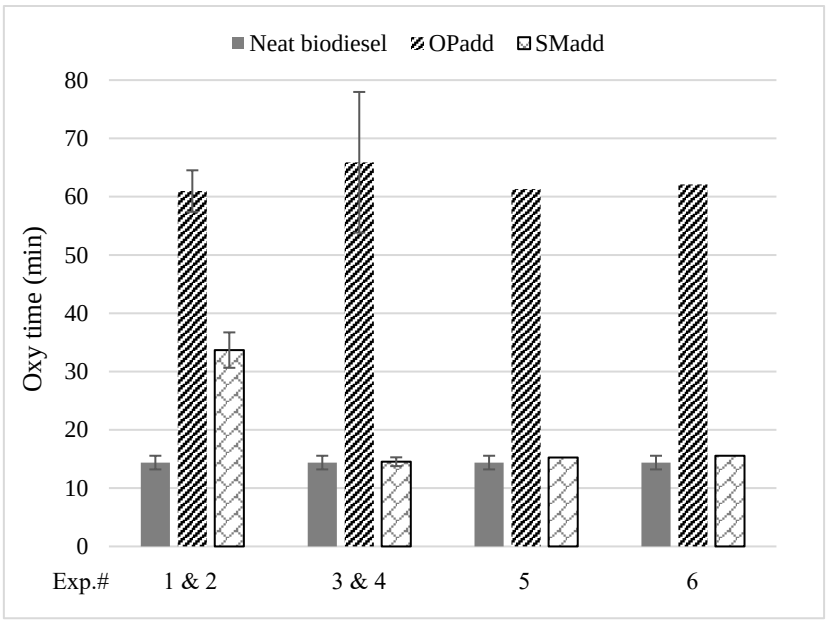

Figure 3: Oxidation stability time of neat and dopped biodiesel.