Journal of Engineering Research

THE INFLUENCE OF AC AND NI/AC CATALYST IN THE ANTIOXIDANT ADDITIVES PRODUCTION FROM ARGAN SHELLS LIGNIN

Zainab Afailal
Thermochemical Processes Group, Aragón Institute of Engineering Research (I3A), Universidad de Zaragoza
Zaragoza, Spain
0000-0002-9091-672X

Noemí Gil-lalaguna
Thermochemical Processes Group, Aragón Institute of Engineering Research (I3A), Universidad de Zaragoza
Zaragoza, Spain
0000-0002-8704-9274

Andrea Vanzella
Dipartimento di ingegneria civile, chimica, ambientale e dei materiali (DICAM), Università Di Bologna, Italy

Jose Luís Sanchez
Thermochemical Processes Group, Aragón Institute of Engineering Research (I3A), Universidad de Zaragoza
Zaragoza, Spain
0000-0002-9705-2207

Abstract: The production of antioxidant additives via the hydrothermal treatment of lignin from argan shells (agricultural waste) was evaluated in the current study. Specifically, the effect of using a Ni catalyst supported on activated carbon which had been prepared from the same waste (argan shells), has been studied. Adding activated carbon (without Ni load) to the reaction medium slightly improved the additives' production, while no significant effect on its antioxidant activity was observed.

Keywords: Lignin conversion, antioxidant additives, argan shells, waste valorization, biodiesel.

INTRODUCTION

Lignin conversion could be a potential alternative to the petrochemical industry, especially for fuel and chemicals production (Gillet et al., 2017). Lignin is a biopolymer with a complex structure composed of phenyl propanoid groups (guaiacyl, syringyl and hydroxyphenyl) linked by means of C-C and ether bonds (Gillet et al., 2017; Ma et al., 2021). For its chemical valorization, lignin fragmentation can be implemented via various technologies, such as biological depolymerization, catalytical and thermochemical treatments (Ragauskas et al., 2014). Several studies of lignin depolymerization have demonstrated that hydrothermal processes could be a promising way to produce aromatic molecules of a reduced size, such as monomers, dimers and trimers. These phenolic molecules showed to be promising and sustainable feedstock to produce additives with a great potential antioxidant activity (Afailal et al., 2021).

Biodiesel is essentially composed of fatty acid monoalkyl esters (FAME), which are synthesized through the transesterification of triglycerides with a simple alcohol (Yaakob et al., 2014). Biodiesel tends to be less resistant to oxidative degradation than fossil diesel due to the instability caused by the unsaturation of fatty acid chains (Pullen and Saeed, 2012). Hence, the main role of the antioxidant additives is to prevent the formation of peroxyl radicals by substituting them with less reactive radicals to stop this chain degradation. Therefore, phenolic compounds have previously been shown to be effective sustainable antioxidants for biodiesel (Lavoie et al., 2019).

In a previous work, the lignin-rich fraction was extracted from argan shells (AS) by the semi-chemical soda pulping (Afailal et al., 2021); this material is an agricultural waste rich in lignin proceeding from argan oil production. The extracted lignin-rich fraction was hydrothermally treated in H_2, CO_2 and HCOOH reaction mediums to produce antioxidant additives for biodiesel. Incorporating these additives led to significant improvements in the oxidation stability (up to 400 %).

In order to continue in the same research line, the current work also addresses the hydrothermal treatment of the same extracted lignin-rich fraction (from AS) introducing to the reaction medium, this time, activated carbon (AC) or nickel catalyst supported on activated carbon (Ni/AC). The effect on the yield and characteristics of the antioxidant additive was outlined. The activated carbon used in the catalyst preparation was produced by AS pyrolysis (at 450 °C) and subsequent activation with CO_2 (at 900 °C). This involves another valorization route to be explored for this waste.

MATERIALS AND METHODS
MATERIALS

Argan shells (AS) were provided by an argan oil cooperative in southwest Morocco. Table 1 summarizes the characteristics of the raw material. Analytical standards and methods

used in the feedstock characterization are also detailed in Table 1. As can be seen, AS is a material rich in lignin (up to 34 wt. %) with a low ash content (0.3 wt. %) and considerable HHV (19 MJ/kg). Carbon and oxygen contents are pretty similar (47 wt.%).

Additionally, as shown in Table 1, the lignin fraction extracted from AS (ASL_f) by semi-chemical pulping was characterized by high ash content (up to 60 wt.%) compared with initial ash content in AS (0.3 %). The use of NaOH in the pulping treatment could explain this. The presence of NaOH could be beneficial to the hydrothermal treatment of ASL_f as it could be considered a base catalyst in the process (Otromke et al., 2019). While on an ash-free basis, the C content in ASL_f was up to 75 wt.%, H content of 8 wt.% and O content of 16 wt.%.

Finally, as mentioned above, in addition to the ASL_f, activated carbon (AC) from AS as well as Ni catalyst supported on this activated carbon were also involved in this study. Hence, Table 2 resumes their main characteristics.

Parameter	AS	ASL_f	Analytical standards/methods or equipment
Proximate analysis (wt. % ar. basis)			
Ash	0.30 ± 0.01	60.1 ± 0.5	EN 14775:2010
Moisture	6.5 ± 0.1	n.d	EN 14774-3:2010
Volatile matter	75.7 ± 0.1	n.d	EN 15148:2010
Fixed Carbon	17.5 ± 0.2	n.d	By difference
Ultimate analysis (wt. % ar. basis)			
C	47.5 ± 0.2	29.4 ± 0.1	LECO CHN628
H	6.5 ± 0.1	3.04 ± 0.04	LECO CHN628
N	0.177 ± 0.003	0.23 ± 0.02	LECO CHN628
O	45.5 ± 0.2	7 ± 1	By difference
HHV (MJ/kg)	18.98 ± 0.02	10.33 ± 0.04	Calorific Bomb IKA C2000 basic
Chemical composition (wt. % ar. basis)			
Extractives	0.2 ± 0.1	n.d	Soxhlet extraction using CH_2Cl_2
Hemicellulose	21 ± 1	n.d	Van Soest digestion
Cellulose	35 ± 2	n.d	Van Soest digestion
Lignin	34 ± 2	n.d	Van Soest digestion

n.d: no determined

Table 1: Ultimate and proximate analyses, HHV and chemical composition of AS and ASL_f.

	AC	Ni/AC
Ultimate analysis (wt.% ar. basis)		
C	94.9 ± 0.3	82.7 ± 0.3
H	0.55 ± 0.04	<0.05
N	1.0 ± 0.1	<0.05
O*	2.0 ± 0.1	n.d
Ash	1.5 ± 0.2	22.2 ± 0.1
Textural characterization		
S_{BET} (m²/g)	1149 ± 64	797.5
Micropore volume (cm³/g)	0.42 ± 0.02	0.3
Average pore size (nm)	0.86 ± 0.03	0.87

* by difference

Table 2: Characterization of AC and Ni/AC.

EXPERIMENTAL METHODS AND ADDITIVES PREPARATION

Depolymerization of ASL_p, dissolved in water at a concentration of 7 wt.%, occurred under hydrothermal conditions in a 500 mL stainless steel stirred Parr reactor 4575 (Figure 1). First, the process was carried out without catalyst loading, and then, the effect of adding AC or Ni/AC at different mass ratios was evaluated. Ni/AC catalyst was also tested under an H_2 atmosphere. Table 3 resumes the operational conditions of all experiments. After adding the corresponding amount of lignin fraction and AC or Ni/AC to the reactor, the latter was sealed and purged many times with N_2 to ensure the absence of air (a common step for all the runs except Exp.#6 where an initial pressure of 25 bar of H_2 was loaded). Subsequently, the reactor was heated up to 300 °C at a heating rate of 5 °C/min and maintained constant for 1 h. Once the experiment had finished, the reactor was quickly cooled by immersing it in an ice bath and circulating tap water into the built-in cooling coil. Once the reactor was open, the aqueous liquid and solid products were recovered from the reactor and filtered. An additional weighted amount of water was used to wash the filtered solid and the reactor walls.

On the one hand, the filtered solid was extracted with methanol in a soxhlet extractor (for 36 h). Hence, the organic fraction obtained from this extraction (soluble in methanol, from now on, SM_{add}) was tested as an antioxidant additive. On the other hand, the filtered liquid was extracted using twice the weight of isopropyl acetate. The mixture (filtred liquid + isopropyl acetate) was shaken for 10 min in a funnel, and then it was left to decant. The decanted aqueous phase was separated and discarded, while the organic phase (OP) was filtered using silicone-treated filter paper to ensure the retention of aqueous phase particles in suspension. After that, the solvent was removed in a rotary evaporator at 60 °C and under vacuum conditions. The remaining dried solid, organic phase additive OP_{add} from now on was weighed for quantification purposes and stored. The additives yields were calculated according to Eq.1a and Eq.1b.

$$Y_{SMadd}\ (wt.\%) = \frac{W_{SM}}{W_{ASLf\ (ash\ free)}} \cdot 100 \quad (Eq.\ 1a)$$

where W_{OP} is the weight (g) of the extracted fraction from the water-insoluble solid after methanol evaporation and W_{ASLf} is expressed on an ash-free basis involving only the organic fraction present in the raw material.

$$Y_{OPadd}\ (wt.\%) = \frac{X_{OP} \cdot W_{OP} \cdot W_{FL}}{W_{EL} \cdot W_{ASLf\ (ash\ free)}} \cdot 100 \quad (Eq.\ 1b)$$

where X_{OP} is the concentration (wt. %) of the lignin-derived compounds in the OP, W_{OP} is the weight (g) of OP obtained after the extraction, W_{FL} is the weight (g) of the filtred liquid, and W_{EL} is the weight (g) of the aqueous liquid subjected to extraction.
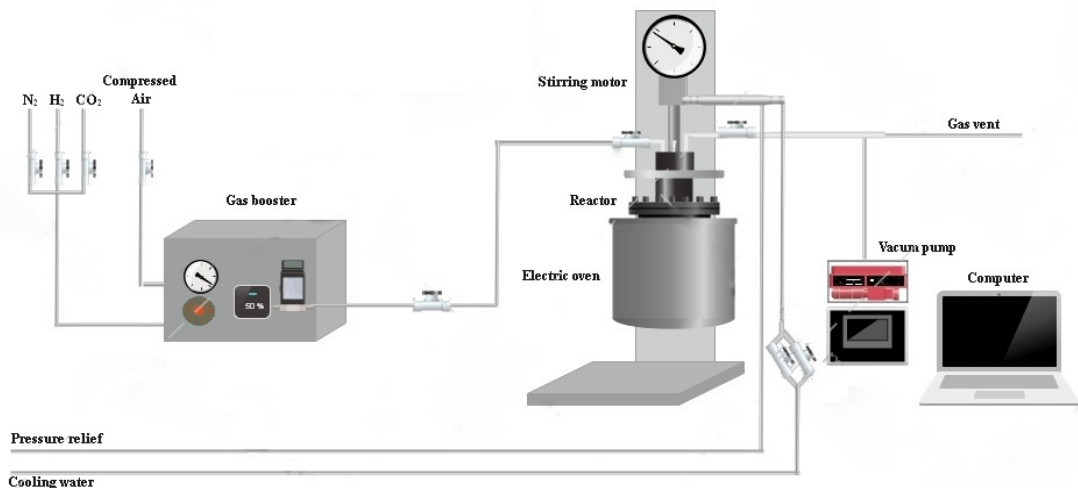
Figure 1: Hydrothermal experimental setup (Parr reactor).

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

Table 3: Operational conditions in the experiments of ASL depolymerization.

BIODIESEL ADDITIVATION AND MEASUREMENT OF OXIDATION STABILITY

Neat biodiesel prepared from sunflower oil was initially doped with 1 wt.% of the dried additives. The biodiesel production process has been described in greater detail elsewhere (García et al., 2017; Gil-Lalaguna et al., 2017; Lavoie et al., 2019; Palomo et al., 2019). 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 by evaporation. The remaining biodiesel + additive was centrifuged in order to separate the insoluble fraction of the additive. The doped biodiesel was recovered, while the insoluble fraction remaining at the bottom of the centrifugation tube was thoroughly washed with hexane (with sonication) to remove biodiesel traces. The washed solid was dried overnight at 50 °C and weighed to determine the dosage of the additive that was really dissolved in biodiesel (calculated by Eq.2).

$$Real\ dosage\ of\ soluble\ additive\ (\%) = \frac{W_{initial\ additive} - W_{insoluble\ additive}}{W_{biodiesel} + (W_{initial\ additive} - W_{insoluble\ additive})} \cdot 100 \quad (Eq.2)$$

where $W_{initial\ additive}$ is the weight (g) of additive initially added to biodiesel, $W_{insoluble\ additive}$ is the weight (g) of insoluble additive quantified after centrifugation, hexane-washing and drying, and $W_{biodiesel}$ is the weight (g) of neat biodiesel used for the mixture.

Both before and after the dopping, biodiesel oxidation stability was measured according to EN 16091 and ASTM D7545 methods utilizing a PetroOXY device.

Briefly, the method consists in measuring the time for a 10 % drop of the oxygen pressure

in contact with the biodiesel sample at 140 °C. Then OXY times obtained for neat and doped biodiesel samples were compared to calculate the oxidation stability improvement rate (ΔOXY) (Eq.3).

$$\Delta OXY\ (\%) = \frac{OXY\ doped\ biodiesel - OXY\ neat\ biodiesel}{OXY\ neat\ biodiesel} \cdot 100 \qquad \text{(Eq. 3)}$$

RESULTS AND DISCUSSION

HYDROTHERMAL TREATMENT: PRODUCTS AND ADDITIVES YIELDS

During depolymerization, ASL_f has been mainly converted to water-soluble and water-insoluble solid compounds. Figure 2 shows the yields of both products, calculated over the initial amount of ASL_f fed. Only a minimal amount of gases was generated in the process (less than 3 wt.%). As seen, the main obtained product was the water-soluble solid. 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. The water-soluble solid yielded between 89 and 93 wt.%, and the water-insoluble solid around 5 wt.%.
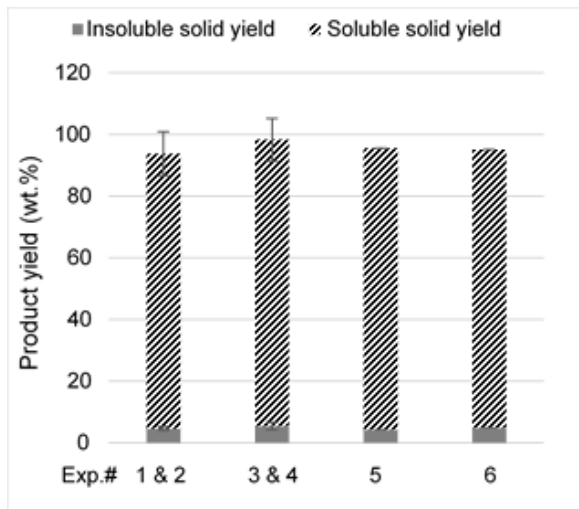

Figure 2: Products distribution.

Differently from the product yields after the experiments, the extracted additives (OP_{add} and SM_{add}) were strongly affected by the operational conditions, as shown in Figure 3. The yield of OP_{add} was enhanced by the presence of the AC or Ni/AC catalyst, from 5 wt.% in Exp.# 1 and 2 to the highest value of 7 wt.% when Ni/AC was introduced to the reaction medium. While an inverse trend was observed for the SM_{add}, its yield decreased in the presence of either AC or Ni/AC (from 6 wt.% without adding AC to 2 wt.% in the presence of Ni/AC). That could point to the retention of some organic compounds on the AC even after the long soxhlet extraction process or to a different solid nature less extractible with methanol.
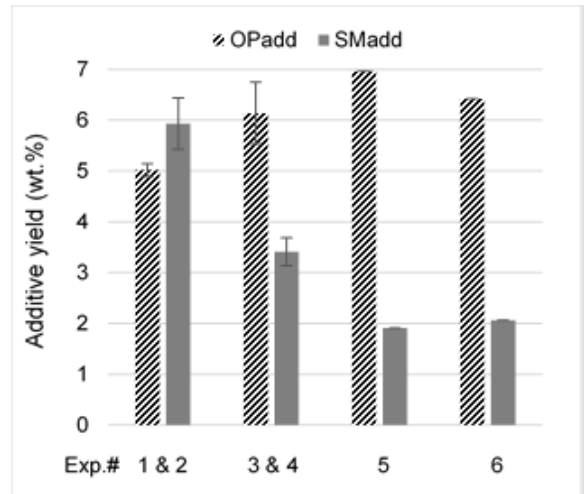

Figure 3: Additives yields.

REAL DOSAGE OF THE ADDITIVE AND OXIDATION TESTS

As stated before, the additive incorporated into the biodiesel was not entirely soluble in most cases. Hence the real dosage of soluble

additive was calculated. For the OP$_{add}$, this parameter was up to 1 wt.% when no AC or Ni/AC was loaded (which means that the additive was totally dissolved in biodiesel). While using AC or Ni/AC, the additive dosage ranged between 0.88 and 0.91 wt.%. On the contrary, in almost all cases, the Sm$_{add}$ was insoluble in biodiesel except the additives obtained without loading AC or Ni/AC, where the real dosage of the additive was up to 0.3 wt.%.

Concerning the antioxidant potential, Figure 4 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 a 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. The additive solubility in biodiesel could be the principal reason.

In terms of oxidation stability improvement, ΔOXY of biodiesel doped by OP$_{add}$ was around 330 % regardless of the operational condition. A slight improvement was observed in the case of Exp.#3 and 4 (358 %) when AC was added (without Ni loading).
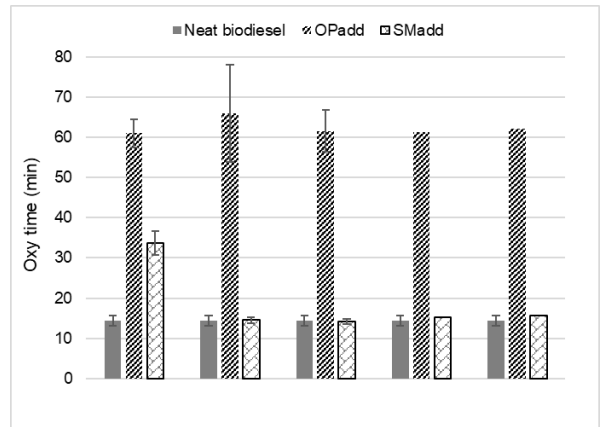

Figure 4: Oxidation stability time of neat and dopped biodiesel.

CONCLUSION

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 additive production, but no significant differences in the additive solubility or its antioxidant potential were found when blended with biodiesel at a small dosage.

The additives produced from the water-soluble solid had a noticeable oxidation stability effect, while the ones prepared from water-insoluble solid were not soluble in biodiesel and with no antioxidant effect. Further experimental work involving other factors, such as the treatment temperature or the reaction time, is required.

REFERENCES

Afailal, Z., Gil-Lalaguna, N., Torrijos, M. T., Gonzalo, A., Arauzo, J., & Sánchez, J. L. 2021. Antioxidant Additives Produced from Argan Shell Lignin Depolymerization. *Energy & Fuels, 35*(21), 17149-17166. doi: 10.1021/acs.energyfuels.1c01705

García, M., Botella, L., Gil-Lalaguna, N., Arauzo, J., Gonzalo, A., & Sánchez, J. L. 2017. Antioxidants for biodiesel: Additives prepared from extracted fractions of bio-oil. *Fuel Processing Technology, 156*, 407-414. doi: https://doi.org/10.1016/j.fuproc.2016.10.001

Gil-Lalaguna, N., Bautista, A., Gonzalo, A., Sánchez, J. L., & Arauzo, J. 2017. Obtaining biodiesel antioxidant additives by hydrothermal treatment of lignocellulosic bio-oil. *Fuel Processing Technology, 166*, 1-7. doi: https://doi.org/10.1016/j.fuproc.2017.05.020

Gillet, S., Aguedo, M., Petitjean, L., Morais, A. R. C., da Costa Lopes, A. M., Łukasik, R. M., & Anastas, P. T. 2017. Lignin transformations for high value applications: towards targeted modifications using green chemistry. [10.1039/C7GC01479A]. *Green Chemistry, 19*(18), 4200-4233. doi: 10.1039/c7gc01479a

Lavoie, J.-M., Ghislain, T., Bahl, E., Arauzo, J., Gonzalo, A., Gil-Lalaguna, N., & Sánchez, J. L. 2019. Renewable antioxidant additive for biodiesel obtained from black liquor. *Fuel, 254*, 115689. doi: https://doi.org/10.1016/j.fuel.2019.115689

Ma, Z., Kasipandi, S., Wen, Z., Yu, L., Cui, K., Chen, H., & Li, Y. 2021. Highly efficient fractionation of corn stover into lignin monomers and cellulose-rich pulp over H2WO4. *Applied Catalysis B: Environmental, 284*, 119731. doi: https://doi.org/10.1016/j.apcatb.2020.119731

Otromke, M., White, R. J., & Sauer, J. 2019. Hydrothermal base catalyzed depolymerization and conversion of technical lignin – An introductory review. *Carbon Resources Conversion, 2*(1), 59-71. doi: https://doi.org/10.1016/j.crcon.2019.01.002

Palomo, J., Moles, S., Salafranca, J., Gil-Lalaguna, N., Gonzalo, A., & Sánchez, J. L. 2019. Production of antioxidants for biodiesel from straw black liquor depolymerization. *WIT Transactions on Ecology and the Environment, 237*, 97-108. doi: 10.2495/esus190091

Pullen, J., & Saeed, K. 2012. An overview of biodiesel oxidation stability. *Renewable and Sustainable Energy Reviews, 16*(8), 5924-5950. doi: https://doi.org/10.1016/j.rser.2012.06.024

Ragauskas, A. J., Beckham, G. T., Biddy, M. J., Chandra, R., Chen, F., Davis, M. F., Davison, B. H., Dixon, R. A., Gilna, P., Keller, M., Langan, P., Naskar, A. K., Saddler, J. N., Tschaplinski, T. J., Tuskan, G. A., & Wyman, C. E. 2014. Lignin Valorization: Improving Lignin Processing in the Biorefinery. *Science, 344*(6185), 1246843. doi: doi:10.1126/science.1246843

Yaakob, Z., Narayanan, B. N., Padikkaparambil, S., Unni K, S., & Akbar P, M. 2014. A review on the oxidation stability of biodiesel. *Renewable and Sustainable Energy Reviews, 35*, 136-153. doi: https://doi.org/10.1016/j.rser.2014.03.055