

Article

Valorization of Pyrolyzed Biomass Residues for the Transformation of Waste Cooking Oil into Green Diesel

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Abstract: This study aims to utilize biochars derived from residual biomass as supports for Ni-based catalysts. For the preparation of the biochars, byproducts of agro-industrial activities were used, such as espresso coffee residue (C) and rice husks (R). Sufficient quantities of the respective biochars (BioC and BioR) were prepared via pyrolysis at 850 °C of the aforementioned materials under limited oxygen conditions. The biochars were further treated with hot water (WBioC, WBioR), H₃PO₄ or H₂SO₄ solution (BioC-P, BioC-S, BioR-P, BioR-S), and NaOH solution (BioC-A and BioR-A), and the obtained solids were characterized using various physicochemical techniques. The biochars produced were microporous with high surface areas (367–938 m²g^{−1}). The most promising biochars were selected as supports for the preparation of nickel catalysts (10 wt.% Ni) with high Ni dispersion (mean crystal size: 8.2–9.8 nm) and suitable acidity. The catalysts were evaluated in a high-pressure semi-batch reactor for the transformation of waste cooking oil (WCO) into green diesel. The 10Ni-BioC-P catalyst exhibited the best performance, resulting in a complete conversion of the WCO but a low hydrocarbon yield (7.5%). Yield improvement was achieved by promoting this catalyst with molybdenum. The addition of Mo increased the hydrocarbon yield by almost three times (19.5%).

Keywords: biochar; nickel catalyst; green diesel; renewable diesel; spent coffee grains; rice husk; biochar post-treatment



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1. Introduction

Active carbon (AC) has been a material of great scientific and technological interest in recent years. It is commonly used in filters (gas and water) and as a catalytic support. Active carbon derived from the pyrolysis of biomass (300–1300 °C) is called biochar [1]. Biochars produced from biomass residues are low cost materials, and their utilization contributes to the circular economy [2,3]. The chemical and physical properties of different biochar types depend on the kind of rough material and the production method [4].

Many studies have focused on the ability of biochars to remove water pollutants via adsorption [5,6] and advanced oxidation processes [7,8]. Several studies have also shown that biochar increases crop yields through soil amendment [9] and removes NO_x and SO₂ in flue gas [10,11].

From a catalytic point of view, biochars are of particular interest because they contain inorganic components (mainly P, Ca, Mg, and K) that can act as modifiers or promoters of the final supported catalysts. Biochar-supported Ca, Na, and K catalysts find applications in transesterification reactions [12–14]. On the other hand, catalysts of transition metals

supported by biochars are commonly used for transesterification, reforming, Fischer–Tropsch synthesis, hydrogenation/dehydrogenation, and isomerization reactions [1,15–19]. Recently, R. Ramos (2022) and co-workers have presented an extensive review of the field [20].

The presence of various functional groups on the surface of biochars (mainly $-C=O$, $-COOH$, $-C=O$, and $-OH$) can affect their supporting properties and/or the catalytic behavior of the final supported catalysts [21]. Moreover, biochars usually exhibit a relatively high specific surface area and significant porosity in the range of micropores. These characteristics depend on both the kind of raw biomass and the pyrolysis conditions [22]. The latter characteristic makes it difficult to utilize these materials as catalyst supports when large molecules are involved in the catalytic processes. In order to overcome this drawback, the initial biochars are further processed to obtain meso-pores [23,24].

Metallic Ni catalysts supported by various supports exhibit important catalytic activity for the transformation of vegetable oils and animal fats into green diesel via hydrotreatment, where selective deoxygenation (SDO) takes place [25]. SDO processes involve the saturation/hydrogenation, hydrogenolysis, and oxygen removal of the following:

- Water through the hydrodeoxygenation (HDO) of intermediate alcohols;
- CO through the decarbonylation of intermediate aldehydes (deCO);
- CO₂ through the decarboxylation (deCO₂) of intermediate fatty acids [25].

The SDO mechanistic scheme, given elsewhere [26], shows that esterification reactions between intermediate fatty acids and fatty alcohols also lead to the formation of wax esters. The SDO of the latter is one of the slowest steps of the process [27]. Carbon-supported catalysts favor the deCO pathway [28]. The support supplies acid and basic sites, and thus, a synergy is developed between them and the metal sites, which is essential for the SDO process.

In the context of a circular economy, we used biochars produced from waste biomass as supports for Ni-based catalysts. The use of waste and renewable materials as catalyst supports increases the sustainability of the process [29]. Waste espresso coffee grains and a rice husk were used as rough materials for biochar preparation via pyrolysis under restricted oxygen conditions. The world production of waste coffee grains and rice husks is estimated at 5.59 and 100 million tons/year, respectively [30,31]. The exploitation of these renewable and waste materials is of crucial importance from an environmental point of view. Various methods have been used in the improvement of the physical and chemical characteristics of biochars [32]. In the present study, hot water, acid, and alkaline treatments of the biochars were applied to the target to improve mainly the biochars' textural characteristics. Based on these characteristics, some of the materials obtained were selected as supports for the preparation of metallic Ni catalysts with 10 and 30 wt.% Ni loading as well as a Ni catalyst promoted with Mo. The catalysts were evaluated in a high-pressure semi-batch reactor for the transformation of WCO into green diesel via hydrotreatment under solvent-free conditions. The prepared biochars and catalysts were characterized using various physicochemical methods (pH-equilibrium, N₂-physisorption, XRD, SEM, H₂-TPR, and NH₃-TPD) in order to find correlations between catalyst performance and its physicochemical properties.

2. Results and Discussion

2.1. Morphology and Texture of Raw Materials and Biochars

2.1.1. Biochars Based on Espresso Coffee Residue

As already mentioned, the kind of raw material and the production method influence the physicochemical properties of produced biochars. The pyrolysis of spent coffee grains (C) and a rice husk (R) at 850 °C under limited oxygen conditions for 1 h resulted in the corresponding biochar samples denoted as BioC and BioR, respectively.

The scanning electron microscopy (SEM) technique was used to study the morphology of the obtained materials. Figure 1 illustrates microphotographs of the original espresso coffee residue (C) and the samples obtained via pyrolysis (BioC) and further post-

treatments with hot water (WBioC) or hot solutions of H_3PO_4 (BioC-P), H_2SO_4 (BioC-S), and NaOH (BioC-A).

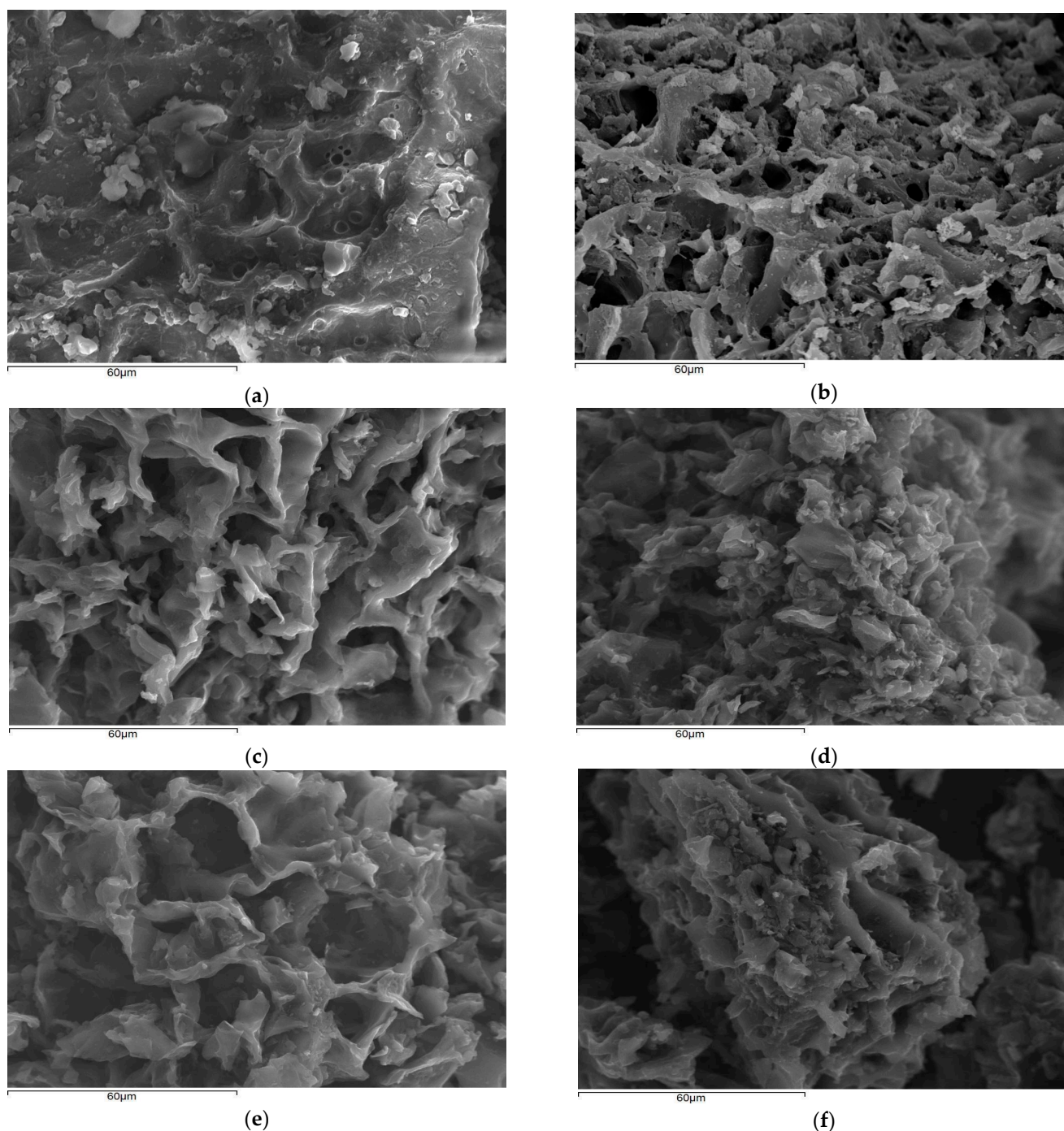


Figure 1. SEM microphotographs of (a) the espresso coffee residue (C), (b) BioC, (c) WBioC, (d) BioC-P, (e) BioC-S, and (f) BioC-A.

These micrographs indicate a change in the morphology of the C sample after pyrolysis, as a porous structure appeared in BioC (Figure 1b). It seems that the post-treatment of BioC did not significantly change its morphology. However, a careful inspection of the corresponding microphotographs reveals that post-treatment lead to the removal of some small particles (probably ash) present inside the pores. Moreover, the treatments with H_3PO_4 (Figure 1d) and NaOH (Figure 1f) solutions caused some extra roughness on the pore walls.

Nitrogen adsorption-desorption isotherms recorded on the espresso coffee residue (C) showed that this sample was non-porous. In contrast, the BioC and the corresponding post-treated samples were porous, and the determined isotherms are shown in Figure S1 included in the Supplementary Material. The shape of these isotherms indicates that all the biochars prepared using espresso coffee residue as raw material were mainly microporous materials with some small-sized meso-pores.

Indeed, the pore size distribution curves illustrated in Figure 2 show that the biochar samples produced from espresso coffee residue exhibited pores with a diameter less than 10 nm independent of their post treatment.

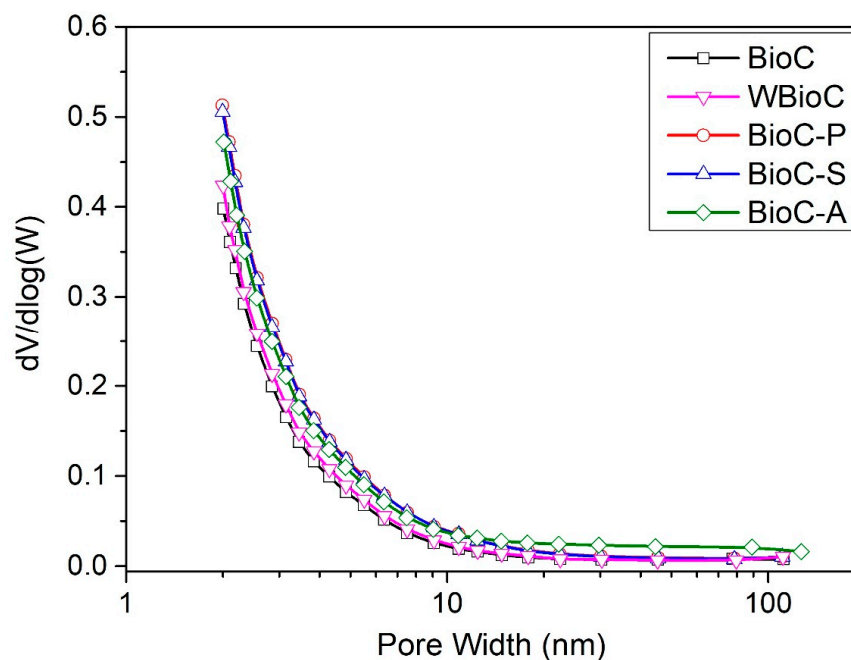


Figure 2. Pore size distributions in the biochars prepared from espresso coffee residue.

Using the isotherms presented in Figure S1, we determined the BET specific surface area of each sample (SSA) as well as the specific surface area of micro-pores (SA_{micro}) and of meso-pores (SA_{exter}) using the t-plot method. Then, the specific pore volume (SPV_{BJH}) and the mean pore diameter (MPD_{BJH}) were calculated using the BJH method. Table 1 indicates the calculated values.

Table 1. Textural characteristics of the espresso coffee residue and the corresponding biochar samples.

Sample	SSA (m^2/g)	¹ SA_{micro} (m^2/g)	² SA_{exter} (m^2/g)	SPV_{BJH} (cm^3/g)	MPD_{BJH} (nm)
C	0.40	–	–	–	–
BioC	752	514	238	0.39	3.1
WBioC	858	603	255	0.44	3.2
BioC-P	921	626	295	0.49	3.4
BioC-S	914	601	313	0.49	3.4
BioC-A	876	603	273	0.47	3.7

¹ Surface area of pores with diameter < 2 nm. ² Surface area of pores with diameter > 2 nm.

An inspection of these values shows that a pyrolysis temperature of 850 °C lead to materials with very high specific surface areas, the main fraction of which were inside the micropores. A hot water treatment of the biochar derived from espresso coffee residue (BioC) provoked an increase in SSA by 107 m^2/g . This is mainly due to an increase in the surface area of micropores by 89 m^2/g . The treatment of BioC with the alkaline aqueous solution (NaOH) resulted in the BioC-A sample, with a slightly larger or similar increase

in the corresponding characteristics (SSA increased by $125 \text{ m}^2/\text{g}$, SA_{micro} increased by $89 \text{ m}^2/\text{g}$, and SA_{exter} increased by $38 \text{ m}^2/\text{g}$). A greater increase in specific surface area was observed in the samples derived via treatment of BioC with acidic aqueous solutions, BioC-P and BioC-S. It is well known that C and O are the main constituents of BioC, accounting for $\sim 96\%$, and only K is another significant element, reaching 2.2% in atomic ratio [33]. The removal of the latter upon the acid post-treatment of BioC could explain the substantial increase in specific surface area observed. However, specific pore volume (SPV_{BJH}) and mean pore diameter (MPD_{BJH}) did not appear to be significantly affected by the various post-treatments applied.

2.1.2. Biochars Based on Rice Husk

Figure 3 shows SEM microphotographs of the residual biomass of a rice husk (R), the resulting biochar (BioR), and the biochars obtained after post-treatment of the latter with hot water (WBioR) or aqueous solutions of H_2SO_4 (BioR-S), H_3PO_4 (BioR-P), and NaOH (BioR-A) at 80°C . There is an obvious change in the morphology of the raw material (Figure 3a) after pyrolysis (Figure 3b), indicating the development of a macroporous texture. Post-treatment of the BioR with hot water and acid or alkaline solutions does not seem to bring about significant changes in its morphology, at least at the micrometric scale.

The N_2 -physisorption experiments showed that the shape of adsorption-desorption isotherms obtained for the biochars produced using rice husk residue (Figure S2) indicates a microporous-mesoporous structure, which remained almost intact after post-treatment with hot water or acid solutions. In contrast, it changed significantly after alkaline treatment. In the latter case, a higher N_2 volume was adsorbed, indicating an increase in pore volume. This is confirmed by the pore size distribution curves obtained via the elaboration of adsorption isotherms (Figure 4).

Figure 4 shows that the alkaline treatment led not only to an increase in the volume of the micro-pores ($<2 \text{ nm}$), but also to the formation of meso-pores ($2\text{--}50 \text{ nm}$) with different diameters. It is well known that rice husk biochar is a reach in Si material [34]. Aqueous sodium hydroxide (NaOH) solution is frequently used for desilication of silica-containing materials (e.g., zeolites) [35]. Thus, desilication of BioR upon alkaline post-treatment could easily explain the creation of new micro- and meso-pores (Figure 4) and the increase in the SPV_{BJH} value (see below Table 2).

Using the isotherms of Figure S2, the textural characteristics of biochars obtained from the rice husk residue have been calculated and presented in Table 2. Inspection of the corresponding values confirms that the pyrolysis of the rice husk residue resulted in a microporous-mesoporous biochar (BioR) with a total specific surface area of $367 \text{ m}^2/\text{g}$, whereas hot water and acid treatment of the BioR do not seem to affect its texture. On the contrary, alkaline post-treatment resulted in a significant increase in total specific surface area ($938 \text{ m}^2/\text{g}$) due to both the increase in the surface area of micro-pores from 230 to $588 \text{ m}^2/\text{g}$ and meso-pores from 137 to $350 \text{ m}^2/\text{g}$. The total pore volume is also increases from 0.23 to $0.67 \text{ cm}^3/\text{g}$, but without significant change in mean pore diameter (MPD_{BJH}).

Table 2. Textural characteristics of the rice husk and the corresponding biochar samples.

Sample	SSA (m^2/g)	¹ SA_{micro} (m^2/g)	² SA_{exter} (m^2/g)	SPV_{BJH} (cm^3/g)	MPD_{BJH} (nm)
R	0.53	0.31	0.22	0.0011	-
BioR	367	230	137	0.23	4.3
WBioR	378	231	147	0.25	4.7
BioR-P	386	235	151	0.25	4.8
BioR-S	382	231	151	0.25	4.8
BioR-A	938	588	350	0.67	5.1

¹ Surface area of pores with diameter $< 2 \text{ nm}$. ² Surface area of pores with diameter $> 2 \text{ nm}$.

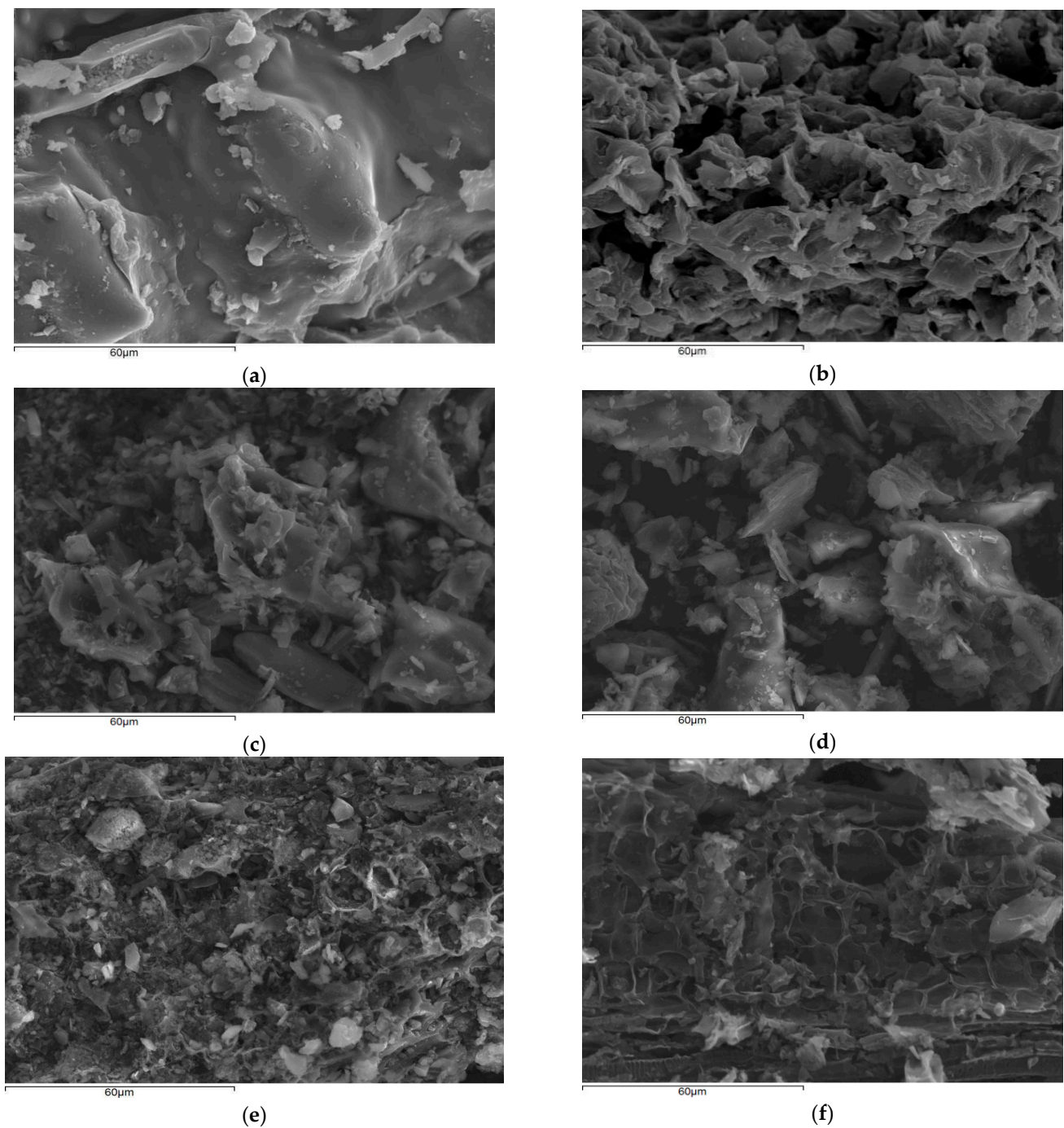


Figure 3. SEM micrographs of a rice husk (a), BioR (b), WBioR (c), BioR-P (d), BioR-S (e), and BioR-A (f).

2.2. Surface Acid-Base Behavior of Raw Materials and Biochars

It is well known that the acid-base characteristics of a catalyst's support influence its supporting properties upon catalyst preparation using an impregnation technique [36]. The acid-base characteristics of the raw biomass and prepared biochars were determined by measuring their equilibrium pH (pH_{eq}). This approach is a simplification of the mass titration method proposed by Noh and Schwarz [37] for point of zero charge estimation. The obtained results are illustrated in Table 3.

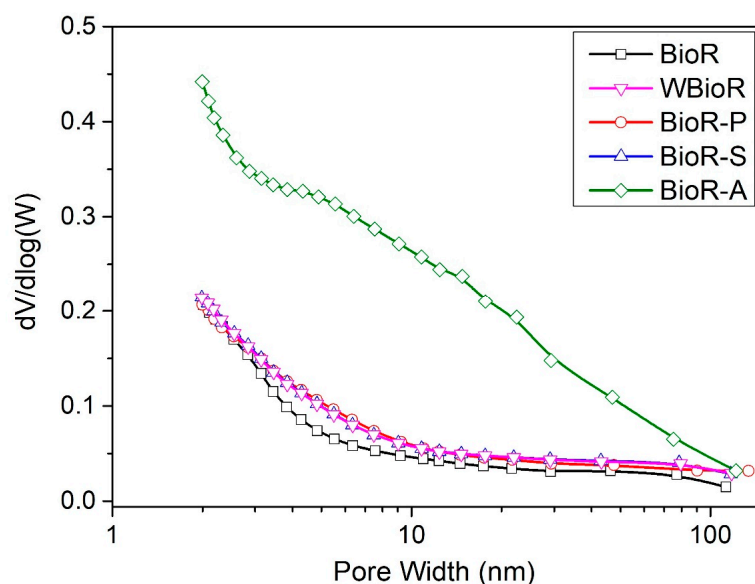


Figure 4. Pore size distributions of the biochars prepared from a rice husk.

Table 3. Equilibrium pH values of the biomass residues and the corresponding biochars.

Sample	pH _{eq}	Sample	pH _{eq}
C	5.48	R	6.00
BioC	10.63	BioR	9.43
WBioC	9.14	WBioR	8.38
BioC-P	5.24	BioR-P	6.22
BioC-S	4.58	BioR-S	6.05
BioC-A	8.82	BioR-A	8.45

Inspection of this table shows that both of the raw biomasses used (C and R) were slightly acidic materials. In contrast, their biochars (BioC and BioR) were alkaline materials, indicating that base components, such as Ca, Mg, and K, are significant. Treatment of these materials with hot water slightly reduced their alkalinity, probably by removing the most easily dissolved alkaline compounds. Acid treatment had a more significant influence on making the materials acidic. The diminution of pH_{eq} values was higher in the case of the samples derived from the BioC treatment than that observed in the case of samples derived from BioR. This is an indication that the concentration of alkaline components is higher in BioC. The extended removal of these components is in good agreement with the significant increase in SSA observed after the acid treatment of BioC (Table 1) and the corresponding low increase observed after the acid treatment of BioR (Table 2). In addition, the almost-no change in pH_{eq} values observed after alkaline treatment is in line with the aforementioned explanation for the change observed after acid treatment.

2.3. Nickel Catalysts Supported on Selected Biochars

Taking into account the above described characteristics and the eco-friendliness of the post-treatment method, we selected WBioC, BioC-P, WBioR, and BioR-A as supports for the preparation of Ni catalysts. Thus, using the wet-impregnation method, we prepared four catalysts containing 10 wt.% Ni (10Ni_WBioC, 10Ni_BioC-P, 10Ni_WBioR, and 10Ni_BioR-A). Textural and geometrical characteristics of the prepared catalysts measured via N₂-physisorption and X-ray diffraction analysis are summarized in Table 4.

Table 4. Textural and geometrical properties of the catalysts.

Catalyst	SSA (m ² /g)	SA _{micro} (m ² /g)	SA _{exter} (m ² /g)	SPV _{BJH} (cm ³ /g)	MPD _{BJH} (nm)	¹ Ni ⁰ _{MCS} (nm)
10Ni_WBioC	719 (858)	436 (603)	283 (255)	0.14 (0.44)	3.5 (3.2)	8.9
10Ni_BioC-P	805 (921)	476 (626)	328 (295)	0.18 (0.49)	3.2 (3.4)	8.2
10Ni_WBioR	300 (378)	160 (231)	140 (147)	0.14 (0.25)	4.6 (4.7)	8.7
10Ni_BioR-A	834 (938)	485 (588)	349 (350)	0.43 (0.67)	5.1 (5.1)	9.8
30Ni_BioC-P	593 (921)	234 (626)	359 (295)	0.23 (0.49)	3.4 (3.4)	21.7
MoNi_BioC-P	883 (921)	494 (626)	389 (295)	0.23 (0.49)	3.5 (3.4)	7.3

¹ Mean crystal size of metallic Ni, calculated using Scherrer equation. Values in parentheses are those of the support used (see Tables 1 and 2).

It is obvious that Ni deposition on the support's surface mainly blocked the micropores of the supports, significantly diminishing their surface area (SA_{micro}) and thus, the SSA and the SPV_{BJH} of the catalysts. However, a slight increase in SA_{exter} was observed in the catalysts supported by biochars derived from espresso coffee residue.

The structural characteristics of the biomass samples used as raw material for biochar preparation, the biochars, the post-treated biochars, and the final Ni catalysts were studied via XRD. Figure 5 illustrates the XRD patterns recorded.

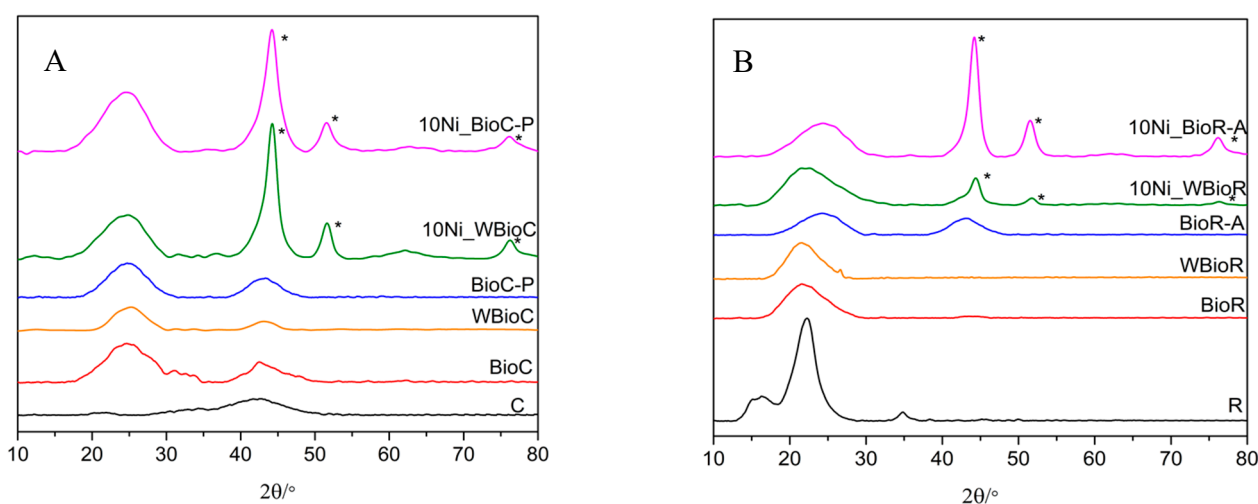


Figure 5. XRD patterns of the initial biomass raw materials, the corresponding biochars, the post-treated biochars, and the synthesized catalysts prepared using (A) espresso coffee residue and (B) a rice husk. *: Ni⁰.

Figure 5A shows that espresso coffee residue is an almost amorphous material. Its pyrolysis resulted in a biochar, the XRD pattern of which presents a wide peak at 2θ: 25° and a smaller one at 2θ: 43.5°. These peaks are characteristic of biochar produced via the high temperature pyrolysis of coffee grains, indicating its amorphous, graphitic nature and the existence of sp² carbon, respectively [38]. The post-treatment of BioC with hot water or phosphoric acid solution and the deposition of nickel phase did not significantly change the support structure. In the XRD patterns of the corresponding catalysts (10Ni_WBioC and 10Ni_BioC-P), three new peaks appear at 2θ: 44.6° (111), 51.8° (200), and 76.3° (220), assigned to the metallic nickel phase [JCPDS 04-0850].

Figure 5B shows that diffractograms of the rice husk (R), BioR, and WBioR exhibit a wide peak centered at about 2θ: 20°, which is characteristic of SiO₂ [39]. This peak is superimposed on the peak ascribed above in the graphitic phase of biochars. After alkaline post-treatment, this peak weakens because of desilication taking place, and the peak of graphitic phase at 2θ: 25° becomes predominant. These are also observed in diffractograms of the nickel catalysts supported on WBioR and BioR-A. In addition, in the XRD patterns of the latter samples, peaks due to the metallic nickel phase are also detected.

The mean crystal size of the nickel phase (Ni^0_{MCS}) was calculated using the peak at 2θ : 51.8° in the Scherrer equation. These values, compiled in Table 4, range between 8.2–9.8 nm, indicating that a very good dispersion of the active phase was achieved in the studied catalysts. However, the 10Ni_BioC-P catalyst exhibits the best Ni dispersion ($\text{Ni}^0_{\text{MCS}} = 8.2$ nm). This could be attributed to the highest surface area of its support and its low pH_{eq} value. Both enhance metal-support interactions upon impregnation [36].

2.4. Reducibility Study

All catalysts studied in this work were reduced at 450°C . This reduction temperature was chosen on the basis of reducibility studies via hydrogen temperature programmed reduction (H_2 -TPR) experiments. Figure 6 shows the corresponding curves. Inspection of this figure reveals that the supports (biochars) underwent reduction in a wide temperature range starting at about 450°C and presenting maximum hydrogen consumption in a range around 650°C . This behavior has been attributed to both the reduction of oxygen-containing groups of biochars and their gasification [40].

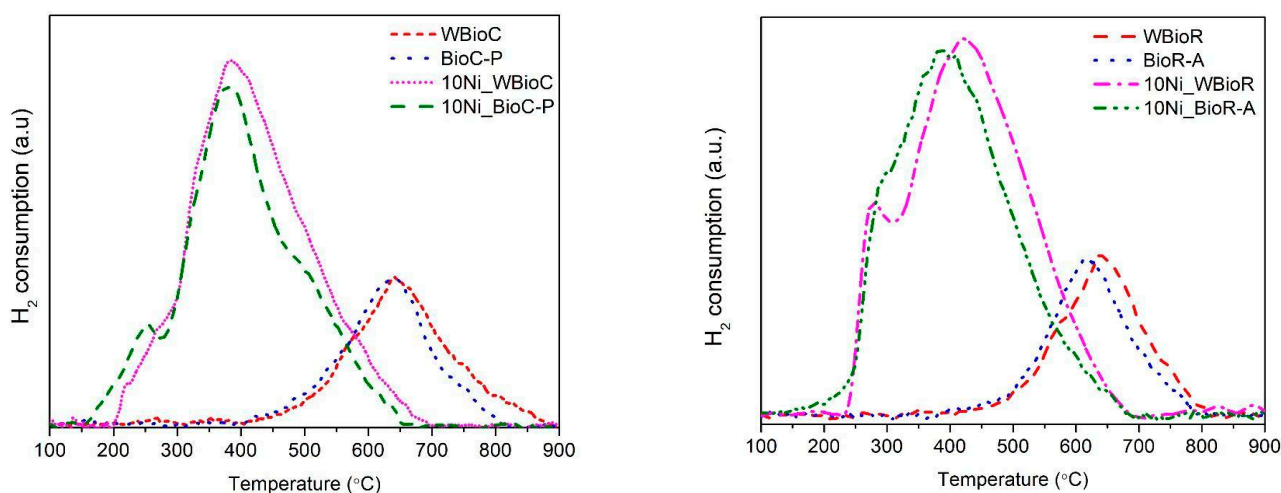


Figure 6. H_2 -TPR curves of catalysts containing 10 wt.% nickel and their respective supports.

The shapes and the positions of reduction curves became very different after the deposition of Ni on the biochar surfaces. Hydrogen consumption started at a very low temperature, and the corresponding curves show a shoulder at 250°C attributed to the reduction of NiO weakly interacting with the support [27]. The reduction curves of the catalysts appear maximal when in the range of 350 – 450°C , indicating the existence of NiO species interacting stronger with the support [41]. The reduction curves of the catalysts are completed with a shoulder appearing at higher temperatures, which could be attributed to the reduction and gasification of the support promoted by the metallic nickel already formed. Based on the above findings, the catalysts' reduction temperature (450°C) was selected in order to ensure the complete reduction of the nickel oxide phase and avoid destroying the support.

2.5. Ni Catalyst Performance

The prepared catalysts were evaluated for the transformation of WCO to green diesel under solvent free conditions using a semi-batch reactor working at 40 bar pressure in 310°C , continuously fed with 100 mL/min H_2 .

Figure 7 shows the conversion achieved over each catalyst as well as the composition of the liquid product. The latter consists of linear hydrocarbons (n-alkanes) with 15–18 carbon atoms (green diesel), unreacted WCO, and intermediate reaction products (mainly free fatty acids, wax esters, and fatty alcohols). The compounds of the latter category are denoted as "others." The produced green diesel presents a high cetane number (70–90) but a very high pour point (21°C) [42].

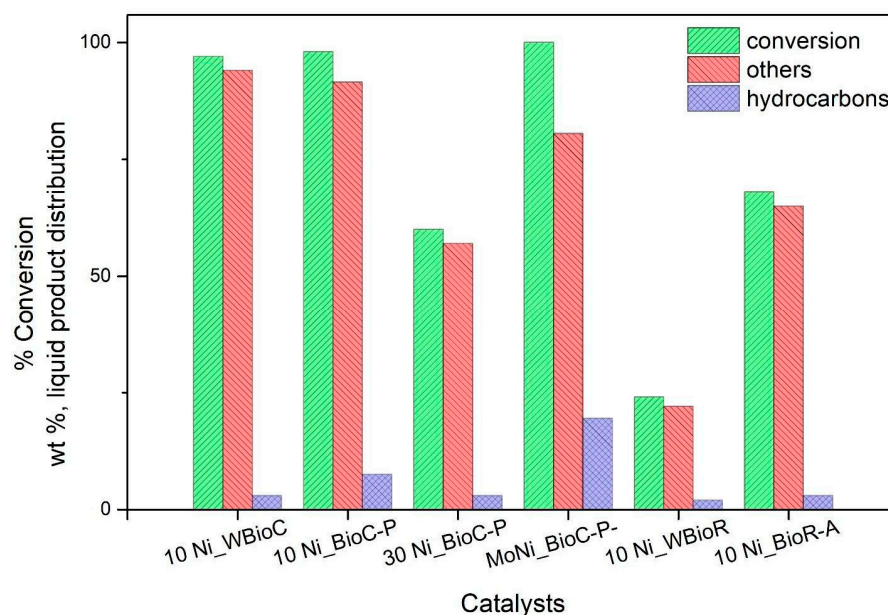


Figure 7. Conversion of WCO and liquid product distribution achieved over the catalysts studied. Reaction conditions: WCO/catalyst ratio = 100 mL/g, pressure = 40 bar, temperature = 310 °C, H₂ flow rate = 100 mL/min, and time = 9 h.

The BioC-supported catalysts (10Ni_WBioC and 10Ni_BioC-P) resulted in an almost complete conversion (98%) of WCO. In contrast, the BioR-supported catalysts (10Ni_WBioR and 10Ni_BioR-A) led to low conversion values. However, in both cases, the hydrocarbon percentage in the product was very low. Among the catalysts with 10 wt.% Ni loading, 10Ni_BioC-P exhibited the best catalytic performance, achieving a hydrocarbon yield of 7.5%. This behavior could be due to the high dispersion of Ni ($\text{Ni}^0_{\text{MCS}} = 8.2 \text{ nm}$) and high SA_{exter} of this catalyst (Table 4), ensuring easier access to reactants on the active sites.

Trying to improve the green diesel yield of the above-mentioned catalyst, we prepared another one increasing the Ni loading to 30 wt.%. (30Ni_BioC-P). Unfortunately, this proved to be not successful, as the conversion of WCO in the presence of this catalyst did not exceed 60% and the green diesel yield was restricted to 3% (Figure 7). An XRD (Figure S3) analysis and N₂-physisorption (Figure S4) revealed that the increase in Ni loading provoked a decrease in the Ni dispersion (Ni^0_{MCS} increased from 8.2 nm in the 10Ni_BioC-P catalyst to 21.7 nm in the 30Ni_BioC-P one) and SSA of the catalyst, respectively (Table 4). H₂-TPR experiments (Figure S5) confirmed the decrease in Ni dispersion by exhibiting an intense reduction peak at 170 °C, attributed to NiO species interacting very weakly with the support. In addition, NH₃-TPD experiments (Figure S6) revealed that the increase in Ni loading provoked a decrease in catalyst acidity. It is well known that the combination of a high population of Ni-active sites (high Ni dispersion) with acid sites is crucial for the SDO of triglycerides [43]. The aforementioned changes provoked by the increase in Ni loading explain the drastic decrease observed in the 30Ni_BioC-P catalyst performance.

However, thinking that there is still room for improvement in the 10Ni_BioC-P catalyst, we modified it by adding a small amount of Mo. Based on our previous studies [30,44–46], we prepared a Mo-modified 10Ni_BioC-P catalyst. Following the wet co-impregnation method, we added a suitable amount of ammonium heptamolybdate tetrahydrate to the impregnation solution, thus regulating the Ni/(Ni + Mo) atomic ratio at 0.9. The catalyst is symbolized as MoNi_BioC-P. Inspection of Figure 7 shows that the well-established promoting action of Mo on the Ni-based catalysts was manifested. The addition of Mo led to a complete conversion of WCO (100%) and increase in the green diesel yield by almost three times, as the liquid product obtained consisted of 19.5% hydrocarbons.

It is widely accepted that in nickel–molybdenum catalysts, electron transfer from nickel to molybdenum favors the reduction of the latter [26]. This results in the creation of

oxygen vacancies (OVs) on the catalyst surface, which are located in Mo-oxo species with a valence lower than +6 (mainly +5 and +4), even if the reduction of the catalyst takes place at temperatures lower than those required for the reduction of the molybdenum phase in the absence of nickel [47]. OVs are mainly responsible for the promoting action of Mo, as they activate the C-O bond of the intermediate free fatty acids (FFAs) adsorbed on them via their C-OH group. Thus, FFAs are transformed to the corresponding aldehydes via a reduction with atomic hydrogen created via dissociative adsorption on neighboring Ni-sites [26]. In addition, aldehydes can be adsorbed on OVs via the oxygen of their carbonyl group and be reduced, giving the corresponding alcohols. The HDO of the latter results in hydrocarbons with the same number of carbon atoms [48].

The addition of Mo can also cause additional beneficial effects on supported Ni catalysts, further enhancing their performance in green diesel production. Indeed, the XRD analysis of the MoNi_BioC-P catalyst (Figure S7) showed that its Ni dispersion was higher than that observed in the 10Ni_BioC-P catalyst (Ni^0_{MCS} decreased from 8.2 nm in the 10Ni_BioC-P catalyst to 7.3 nm in the MoNi_BioC-P one, see Table 4). The beneficial action of the addition of Mo to the Ni dispersion was also confirmed using an SEM-EDS analysis of the aforementioned catalysts, presented in Figure 8.

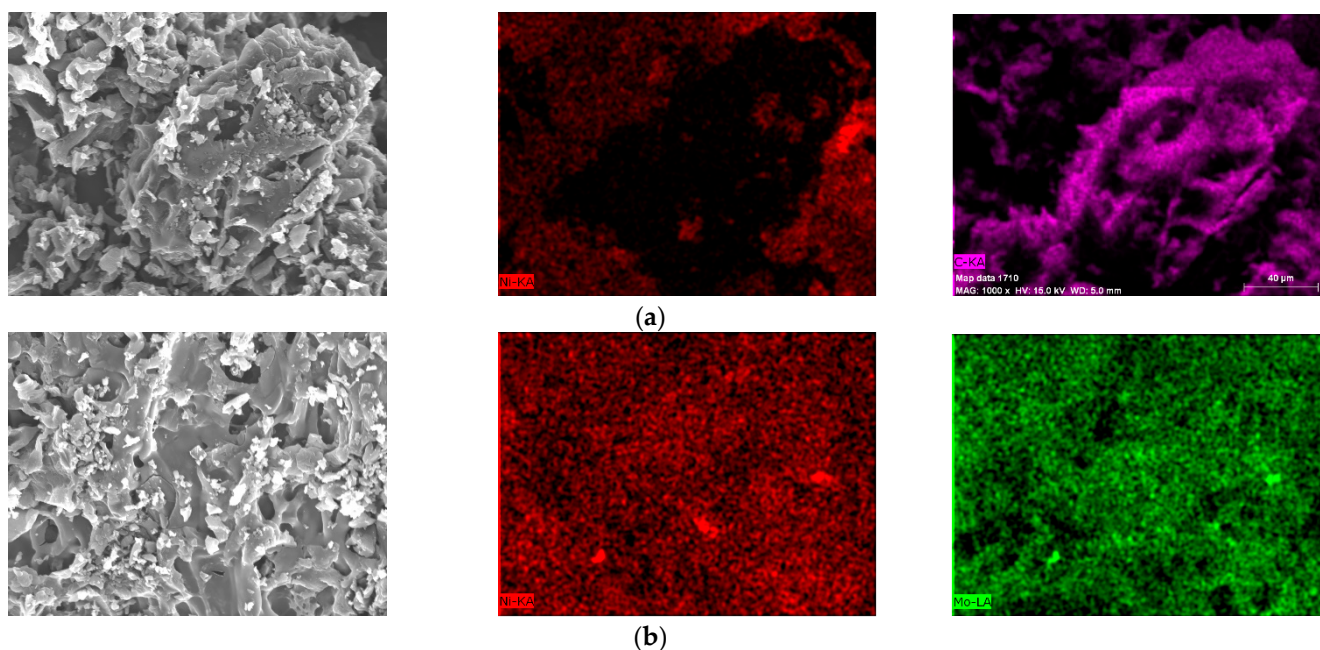


Figure 8. SEM-EDS pictures (Mag.: $\times 1000$), elemental mapping (red: nickel; green: molybdenum; purple: carbon): (a) 10Ni_BioC-P; (b) MoNi_BioC-P.

Moreover, Figure 10 shows that the addition of Mo substantially increases the acidity of the catalyst. Indeed, an inspection of this figure reveals that the addition of Mo increases the population of weak acid sites (low NH_3 desorption temperature), also creating new acid sites of moderate strength (high NH_3 desorption temperature). As already mentioned, the combination of a high population of Ni-active sites (high Ni dispersion) with acid sites is crucial for the SDO of triglycerides [43].

The increase in the Ni dispersion also had a positive influence on the SSA and SA_{ext} of the catalyst (Table 4), as well as on its reducibility (see Figure 9). High dispersion and reducibility increased the population of Ni-active sites.

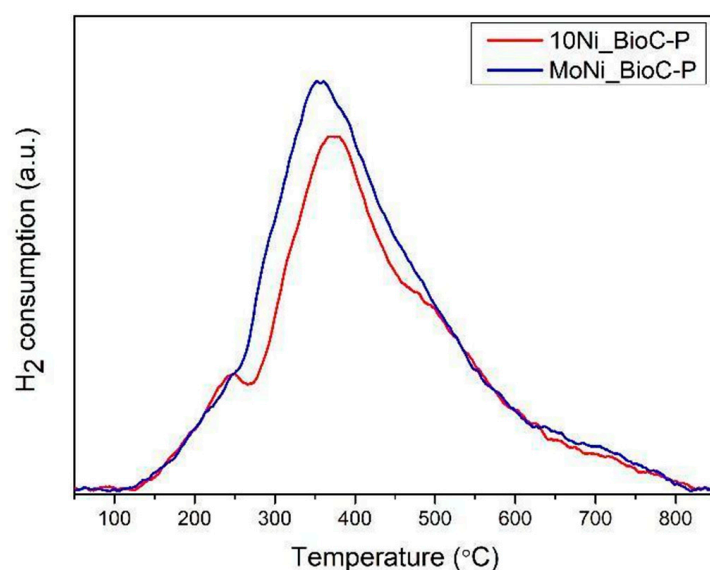


Figure 9. H₂-TPR curves of the MoNi_BioC-P and 10Ni_BioC-P catalysts.

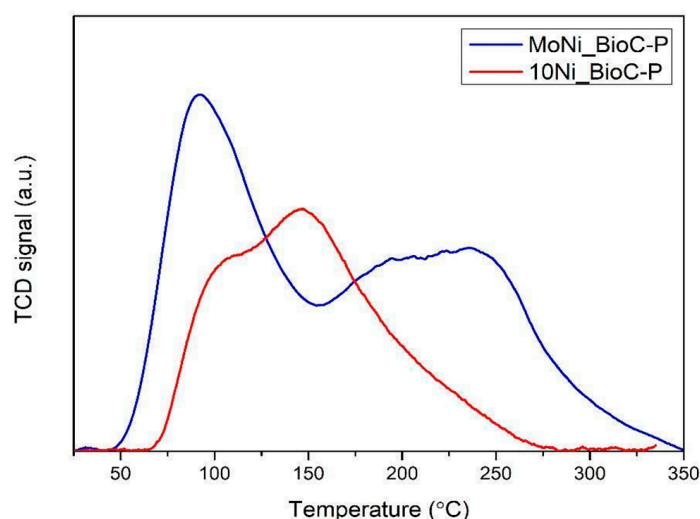


Figure 10. NH₃-TPD curves of the MoNi_BioC-P and 10Ni_BioC-P catalysts.

Closing this section, we have to stress that apart from the catalysts' activity and selectivity, stability is a very important issue for a catalyst's performance. Although we have not performed reusability experiments, the total amount of WCO treated in a catalytic test was equal to 100 mL using 1 g of catalyst with a reaction time equal to 9 h. Such an experiment simulates one performed in a fixed-bed reactor with an LHSV equal to 11.1 h^{−1}, or a similar experiment that adopts a reasonable LHSV value for industrial applications equal to 1 h^{−1} with a duration 100 h time on stream. Preliminary experiments performed in the frame of the present study showed that the hydrocarbon production over Ni or MoNi catalysts supported by biochar increased almost linearly with the reaction time. This is an indication of good catalyst stability.

In a previous work [49], we have found that the addition of Mo to a Ni-catalyst supported by active carbon enhances its stability for the hydrodeoxygenation of phenol. This positive effect has been related to the presence of surface MoO_x species on the Mo-promoted Ni-catalyst. It is well known that the oxides of transition metals create strong acidic surface sites [50], in accordance with our findings (see Figure 10), which are beneficial for SDO reactions. The development of acid sites is related to the comparatively unsaturated Mo^{(6-x)+} species on the surface (Lewis acid sites) [45] and to the hydroxyl groups formed via

the protonation of the terminal Mo = O or the bridging of C–O–Mo bonds on the catalyst surface (Brønsted acid sites) [45]. On the other hand, MoOx species might act as scavengers for coke precursors, protecting the active Ni⁰ phase from deactivation [45]. Based on the above discussion, it is expected that the MoNi_BioC-P catalyst is quite stable for the SDO of WCO.

3. Materials and Methods

3.1. Materials

WCO, kindly offered by Collectoil, Patras, Greece, was used as feedstock. Contained solids were removed via filtration and centrifugation. Its characteristics (density: 0.89 g/mL, static and dynamic viscosity: 9.89 cSt and 0.088 P, acidity: 0.83% oleic acid, iodine number: 67, saponification number: 213, water content: 0.14%, and oligomer content: traces) were determined using methods described elsewhere [51].

The chemicals used were nickel nitrate (Ni(NO₃)₂·6H₂O, Alpha Aesar, Karlsruhe, Germany), ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, Merck, Darmstadt, Germany), an ammonium hydroxide solution (NH₄OH 30%, Carlo Erba Reagents, Val-de-Reuil, France), H₂SO₄ (96%, Penta chemicals, Radiová, Prague, Czech republic), H₃PO₄ (85%, Penta chemicals, Radiová, Prague, Czech republic), NaOH (Merck, Darmstadt, Germany), and tri-distilled water.

3.2. Preparation of the Biochars and the Catalysts

The raw materials used for the production of the biochars as catalyst supports were espresso coffee residue (C) from a cafeteria located on the campus of the University of Patras, Greece, and a rice husk (R) obtained from the company AGRINO SA, Agrinio, Greece. The raw materials, after drying at 110 °C overnight, were placed in a handmade fireproof vessel of 265 mL and transferred to an electric oven (Memmert). The samples were heated at 850 °C (10 °C/min) under conditions of limited oxygen for 1 h. The vessel was then allowed to cool down to room temperature and the biochar was collected. Two biochars were prepared, symbolized as BioC and BioR. Aliquots of the biochars (10 g) were put in spherical flask with a vertical conductor and treated at 80 °C for 4 h with the following: 200 mL of water to prepare WBioC and WBioR; H₂SO₄ solution (2M) to prepare BioC-S and BioR-S; H₃PO₄ solution (2M) to prepare BioC-P and BioR-P; and NaOH solution (2M) to prepare BioC-A and BioR-A. Finally, the acid and alkaline treated biochars were thoroughly washed with hot water and dried overnight at 110 °C.

Nickel catalysts supported by selected biochars were prepared using the wet impregnation method. A total of 5 g of biochar was added to a 50 mL aqueous solution of Ni(NO₃)₂·6H₂O, precisely weighted to obtain supported catalysts with 10 wt.% Ni. A catalyst with 30 wt.% Ni was also prepared. A Mo-promoted Ni catalyst containing 10 wt. Ni and 1.6 wt.% Mo was prepared via wet co-impregnation, adding (NH₄)₆Mo₇O₂₄·4H₂O in the impregnating solution and achieving a Ni/(Ni + Mo) atomic ratio equal to 0.9 in the final catalyst. The catalysts were dried overnight at 110 °C and activated with H₂ (30 mL/min) at 450 °C for 2.5 h. More details of catalyst activation are given elsewhere [45].

3.3. Characterization of the Biochars and the Catalysts

The prepared biochars and catalysts were characterized via N₂-physisorption (Tristar 3000 porosimeter, Micromeritics Instrument Corporation, Norcross, GA, USA), X-ray diffraction (D8 Advance diffractometer, Bruker, Billerica, MA, USA), scanning electron microscopy (SEM-EDS, Zeiss Supra 35 VP FEG, Zeiss, Jena, Germany, equipped with energy dispersive microanalyzer, Bruker, Billerica, MA, USA), H₂-temperature programmed reduction (lab made apparatus), NH₃-temperature programmed desorption (lab made apparatus), and the determination of the equilibrium pH of biochar/water suspension. Details have been given elsewhere [52].

3.4. Evaluation of the Catalysts

The catalysts were evaluated in a semi-batch reactor (Autoclave) for the transformation of WCO into green diesel using 100 mL of WCO and 1 g of the activated catalyst under solvent-free conditions at 310 °C, with an H₂ flow of 100 mL/min and a pressure of 40 bar for 9 h. More details have been given elsewhere [52].

4. Conclusions

Biochars produced via the pyrolysis of espresso coffee residue (BioC) and a rice husk (BioR) exhibited high surface areas (752 and 367 m²g^{−1}, respectively), thus being promising materials for catalyst support. The post-treatment of BioC with a phosphoric acid solution and BioR with a sodium hydroxide solution further improved their characteristics, increasing their SSA values to 921 and 938 m²g^{−1}, respectively.

A nickel catalyst (10 wt.% Ni) supported by BioC and post-treated with a hot H₃PO₄ solution exhibited quite interesting performance in the SDO of WCO (98% conversion, but a low hydrocarbon yield 7.5%). The addition of Mo considerably improved the catalytic performance, increasing the hydrocarbon yield by three times (19.5%). This improvement has been attributed to the following: (i) an increase in catalyst SSA from 805 to 883 m²g^{−1}, (ii) an increase in Ni⁰ dispersion, (iii) an increase in the population of acid sites, and (iv) a synergy between nickel sites and oxygen vacancies (OVs) located on reduced molybdenum oxides present on the catalyst surface.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13061004/s1>, Figure S1: N₂ adsorption-desorption isotherms of the biochar samples obtained via pyrolysis and post treatment of espresso coffee residue; Figure S2: N₂ adsorption-desorption isotherms of the biochar samples obtained via pyrolysis and post treatment of rice husk residue; Figure S3: XRD patterns of the 10Ni_BioC-P and 30Ni_BioC-P catalysts (*: Ni⁰); Figure S4: N₂ adsorption/desorption isotherms determined over 30Ni_BioC-P catalyst; Figure S5: H₂-TPR curves of the 10Ni_BioC-P and 30Ni_BioC-P catalysts; Figure S6: NH₃-TPD curves of the catalysts 10Ni_BioC-P and 30Ni_BioC-P; Figure S7: XRD patterns of the MoNi_BioC-P and 10Ni_BioC-P catalysts (*Ni⁰).

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