Towards Biowastes Valorization. Peanut Shell as Resource for Quality Chemicals and Activated Biochar Production.

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Research

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The purpose of this work was to valorize a regional biowaste through a modest thermo-catalytic pyrolysis process. ZSM-11 zeolites modified by Ni incorporation (1-8 wt%) were synthesized and characterized by means of X-Ray Diffraction, Inductively Coupled Plasma Atomic Emission Spectroscopy, Infrared Fourier Transform Spectroscopy, UV–vis Diffuse Reflectance Spectra and Temperature Programmed Reduction. Results demonstrated that Ni was mainly incorporated as oxide. These porous materials were evaluated as heterogeneous catalysts to improve biooil composition. In this sense, higher hydrocarbon yields and quality chemicals were obtained and oxygenates were diminished. The deactivation of the most active material was studied over six cycles of reaction. In order to achieve the circular bioeconomy postulates, the obtained biochar (usually considered a residue) was further valorized through a physicochemical activation. The obtained activated biochars were extensively characterized.

**Keywords:** peanut shell, biomass pyrolysis, biooil upgrade, Ni-ZSM-11, activated biochar.

1. **Introduction**

In its 17 Sustainable Development Goals (SDGs), the United Nations promotes the principle of optimum and responsible usage of resources for purposes leading to a convincing transition to a circular economy. The main idea of the so-called circular economy consists in advanced redesigning and technological breakthroughs to minimize waste [1]. From these ideas, the concept of “circular bioeconomy” is proposed to be a more efficient biobased renewable resource management. This term integrates the circular economy principles with the bioeconomy theory [2].
Biomass is a promising alternative to fossil resources since its carbon richness. But considering its importance for food production, a competitive situation should be avoided. In this sense, agricultural wastes are ideal candidates for fuels and chemicals production. Peanut is an important grain legume cultivated worldwide with a growing trend of production of about 48 million tonnes [3]. Argentina is the 8th world peanut producer, with around 1,3 million tonnes produced in 2019/2020 campaign. In view of these high quantities, it is important to consider the wastes that peanut processing generates. A 25 wt% of the production corresponds to the shell, a by-product not properly used. Keeping in mind the concept of circular economy, peanut shell (PS) could be consider as the feed of an integral process.

PS contains around 50% cellulose, 20% hemicellulose and 30% lignin [4] that make it difficult to digest and unable as feedstock for animals. Furthermore, biodegradation is extremely low, resulting in the need of severe treatments. Hence, fast pyrolysis seems to be a good alternative in order to treat and give value to this biowaste. In a previous paper [5] we have shown the importance of this thermal process.

As proposed by Dai et al. [6] the use of zeolites as catalysts in pyrolysis reactions could improve hydrocarbons and aromatics yields. Particularly, they have found that Ni modified zeolites promoted pyrolysis vapor deoxygenation and selectivity to aromatic compounds. The use of Ni promoted catalysts in biomass pyrolysis has been studied by many researchers. Most studies focused on ZSM-5, MCM or different oxides [7], but the use of Ni modified ZSM-11 zeolite has hardly been investigated.
As in any production system, biomass fast pyrolysis also generates waste. The solid product of pyrolysis, commonly known as biochar, is usually disposed of and not further utilized. Taking Olofsson and Börjesson [8] ideas, and in order to minimize residues generation, we propose a case of open-loop recycling by employing the biochar in a subsequent system: synthesis of activated biochar (AB). This porous material can be used in Li-ion batteries, gas-phase adsorption or as heterogeneous catalysis.

In this paper, we propose the valorization and recycling of PS in two subsequent product systems. In the first system, PS is considered as renewable C source for platform molecules generation. Considering this biowaste composition, a thermo-catalytic pyrolysis method is proposed. In order to obtain higher hydrocarbons and aromatics yields in the biooil, the effect of Ni-ZSM-11 catalyst is evaluated. The second system employs the residue from the previous one, that is to say biochar, for the synthesis of AB (Figure 1).

2. Experimental section

2.1. Biomass

PS was provided by the company Lorenzati, Ruetsch y Cia., from Córdoba, Argentina. The following pre-treatments were applied to PS: (1) washing to remove soil particles, (2) drying at 105 °C until constant weight, (3) grinding and (4) screening to obtain a PS particle size < 3.35 mm –ASTM E 11/95–. Detailed characterization of biomass has been presented in a previous work [5].

2.2. Catalysts synthesis and characterization
The microporous Na-ZSM-11 zeolite (Si/Al = 23) was prepared by hydrothermal synthesis [9]. Ni-zeolites were prepared by the wet impregnation method. Three concentrations of nickel aqueous solutions (\(\text{NiCl}_2 \cdot 6\text{H}_2\text{O}\), Cicarelli) were used to reach a Ni-content of 1, 5 and 8 wt%. The zeolite was dispersed in the Ni solution at room temperature. Afterwards, the solvent (water) was slowly removed by rotary vacuum evaporation at 80 °C until complete dryness. Finally, the samples were dried at 110 °C overnight and subjected to a thermal treatment consisting of desorption in \(\text{N}_2\) and calcination in air at 500 °C for 8 h. The as-prepared catalysts were named Ni(1)Z, Ni(5)Z and Ni(8)Z, according to metal concentration.

Nickel content was determined by inductively coupled plasma atomic emission spectroscopy with an ICP−OPTIMA Perkin Elmer equipment. The crystalline structure of the catalysts was determined by means of X-ray diffraction (XRD) employing an X’pert PANalytical diffractometer with CuK\(\alpha\) radiation (1.54 Å). The data were collected in 2θ range of 5 – 60° in steps of 0.026° with a count time of 2 s at each point.

Surface area determinations (\(S_{\text{BET}}\)) using Brunauer–Emmett–Teller (BET) method were carried out with \(\text{N}_2\) absorption at 77 K in a Pulse Chemisorb equipment Micromeritics 2700. The \(S_{\text{BET}}\) was determined for fresh and spent catalysts (after the reaction).

Temperature programmed reduction (TPR) studies were done over Ni-zeolites in a Pulse Chemisorb 2720 equipment from Micromeritics. UV–vis diffuse reflectance spectra (UV–vis DRS) in absorbance mode were recorded using a Jasco V 650 spectrometer in the wavelength range 200 to 900 nm.
Infrared Fourier Transform Spectroscopy (FTIR) studies were done to determine acidity of catalysts, employing a Thermo Nicolet iS10. Pyridine was first adsorbed to the materials at room temperature under vacuum conditions and was further desorbed at 250 °C and $10^{-4}$ Torr. Acids sites quantification was done from the bands of 1545 cm$^{-1}$ (Brønsted) and 1450 cm$^{-1}$ (Lewis) using the literature data of the integrated molar extinction coefficients [10].

The amount of coke deposited on the spent catalysts was measured by thermogravimetric analysis (TGA) using a Mettler Toledo thermobalance (TGA/SDTA851e/SF/1100°C). The sample was heated from 25 to 900 °C at a heating rate of 10 °C min$^{-1}$ under 75 mL min$^{-1}$ of air flow. Eq. (1) was used to calculate the relative amount of coke [11].

$$Y_{\text{coke}} \, (\text{wt}) = \frac{m_{100\degree\text{C}} - m_{900\degree\text{C}}}{m_{900\degree\text{C}}} \cdot 100$$

Eq. (1)

Where $m_{100\degree\text{C}}$ and $m_{900\degree\text{C}}$ correspond to the catalyst mass at 100 °C and 900 °C, respectively.

Functional structure of spent catalysts was characterized by XRD and FTIR using the equipment depicted above. In the case of FTIR, the KBr technique was employed.

2.3. Pyrolysis reactions

PS pyrolysis and biooil upgrade were simultaneously carried out in a fixed bed glass reactor (23 mm I.D., 290 mm length) under N$_2$ flow (60 mL min$^{-1}$). For a typical experiment, PS (1 g) was loaded in a glass sample carrier over a catalytic bed. The bed consisted of catalyst (1 g) and milled quartz (7 g). The reactor was introduced in an electric furnace once
the pyrolysis temperature (500 °C) was reached. Condensable vapors were collected at the reactor output in a condenser (<-10 °C). The reactions lasted 10 min. Three repeats of every experimental run were done. Average values are reported.

Eqs. (2), (3) and (4) were used to calculate products yields.

\[ Y_{biochar} (wt\%) = \frac{M_{biochar}}{M_o} \cdot 100 \]  

Eq. (2)

\[ Y_{biooil} (wt\%) = \frac{M_{bio-oil}}{M_o} \cdot 100 \]  

Eq. (3)

\[ Y_{gas} (wt\%) = 100 - [Y_{biooil} + Y_{bio-char} + Y_{coke}] \]  

Eq. (4)

Where, \( M_o \) is the initial mass of the biomass sample (g), \( M_{biochar} \) is the mass of the solid product (g) after the reaction and \( M_{biooil} \) is the mass of the liquid product (g).

Catalyst stability was assessed by using one catalyst sample for six consecutive reaction cycles. Every new reaction was carried out employing the catalyst from the preceding cycle (i.e., the partially deactivated catalyst) maintaining the 1:1 biomass to catalyst mass ratio. Biooil was collected and analyzed after each reaction cycle.

2.4. Products analysis and characterization

Chemical composition of biooil was assessed by the GC-MS technique in a Perkin Elmer Claurus 600 Gas Chromatograph coupled with an ion trap mass spectrometer in full scale mode (m/z 40 to 550). An Elite 5MS capillary column (30 m length, 0.25 mm i.d.) was employed and He was used as carrier gas. Chromatographic peaks were identified by means of NIST MS library and the use of standards. Peak area calibration was accomplished through
specific response factors for each chemical group. The selectivity to each compound was calculated using Eq. (5):

\[ S_i(\%) = \frac{A_i R_i}{\sum_{i=1}^{n} A_i R_i} \times 100 \]

Eq. (5)

Where \( A_i \) is the absolute peak area of compound \( i \) and \( R_i \) is the response factor of compound \( i \).

2.5. Activated biochar synthesis and characterization

AB synthesis was carried out following the protocol published by Fu et al. [12], due to its simplicity and effectiveness. A mechanical mixture of KOH (Strem Chemicals, 85%) and biochar was made in the proportions of 1:1 and 3:1 by weight. The mixture was placed in a fixed bed reactor and submitted to thermal treatment under \( \text{N}_2 \) atmosphere (20 mL min\(^{-1}\)). The heating rate was 20 °C min\(^{-1}\) until 750 °C, maintaining that temperature for 3 h. The as-prepared materials, named AB 1:1 and AB 3:1, were then neutralized and washed with distilled water until pH=7 and dried in an oven at 120 °C until constant weight.

AB yields were calculated employing Eq. (6), where \( M_{\text{biochar}} \) corresponds to the mass of the biochar (g) after the pyrolysis reaction, \( M_{AB} \) is the mass of the as-prepared activated biochar (g) after the synthesis procedure.

\[ Y_{AB} \text{ (wt\%)} = \frac{M_{AB}}{M_{\text{biochar}}} \cdot 100 \]

Eq. (6)

The crystalline structure, FTIR spectra and \( S_{\text{BET}} \) of AB were determined in the equipment depicted above. For FTIR analysis, the samples were prepared by blending a few milligrams of the AB sample with KBr.
Morphological analyses were done by Scanning Electron Microscopy (SEM) employing a microscope FE-SEM Sigma. It was operated at an acceleration voltage of 5 kV. Prior to analysis, the samples were coated with gold. Proximate analysis of AB was also performed using the thermobalance depicted above and following Saldarriaga et al., [13] protocol.

A LabRam spectrometer (Horiba-Jobin-Yvon) coupled to an Olympus confocal microscope was used to obtain the Raman spectra of AB samples. The spectrometer was equipped with a CCD detector at ~ 200 K, the excitation wavelength was 532 nm and the laser power was set at 30 mW.

3. Results and discussion

3.1. Catalysts characterization

The physicochemical properties of the catalysts are shown in Table 1. It can be seen that surface area of fresh materials varied as a function of Ni content. In general, when metal is loaded on porous supports, the surface area decreases due to the pore blockage and metal sintering during the calcination step [14]. $S_{\text{BET}}$ for spent catalysts showed a 23-35% decrease, compared to the fresh samples. It was observed that the reduction in $S_{\text{BET}}$ was bigger when greater the initial $S_{\text{BET}}$ was.

The ICP analysis of the materials confirmed the theoretical Ni quantities, which were in agreement with the experimental results.

| Catalyst | Ni$^a$ | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | Lewis | Brønsted | Total acidity |
|----------|--------|---------------------------------|-------|-----------|--------------|

Table 1. Physicochemical characteristics of the catalysts.
| (%wt) | Fresh | Spent | (μmol Py mg\(^{-1}\)) | (μmol Py mg\(^{-1}\)) | (μmol Py mg\(^{-1}\)) |
|-------|-------|-------|------------------------|------------------------|------------------------|
| HZ    | 0.00  | 378   | 249                    | 7.69                   | 68.79                   | 76.48                   |
| Ni(1)Z| 0.76  | 331   | 260                    | 49.30                  | 61.60                   | 110.91                  |
| Ni(5)Z| 5.40  | 321   | 221                    | 97.97                  | 124.42                  | 222.39                  |
| Ni(8)Z| 7.40  | 287   | 221                    | 52.62                  | 54.68                   | 107.30                  |

\(^a\) Determined by ICP.

The FTIR spectra of the Ni-zeolites samples desorbed at 250 °C are shown in Figure 2a. Bands at 1455, 1492 and 1545 cm\(^{-1}\) can be observed. The band at 1545 cm\(^{-1}\) corresponds to the BAS (Brønsted Acid Sites) formed by the framework Al species through the Si – OH – Al bridge. This band is ascribed to the interaction of pyridinium ion binding on BAS. The band at 1450 cm\(^{-1}\) is related to the LAS (Lewis Acid Sites) formed by the extra framework Al species and electronic defaults in the framework aluminium [15]. The band at 1492 cm\(^{-1}\) corresponds to the vibration of pyridine adsorbed over both LAS and BAS [16].

From Table 1 and Figure 2a it can be seen that the total amount of LAS increased dramatically when the Ni was incorporated to the pristine zeolites. It is well known that the addition of Ni to zeolites modify the acidic properties of the material [17]. The metal can create new LAS associated with Ni\(^{2+}\) and NiO. The highest LAS amount was observed in the sample Ni(5)Z, in accordance to the literature, for similar zeolites [18]. After Ni incorporation, BAS slightly decreased in the case of the Ni(1)Z sample, but were significantly augmented in the case of the Ni(5)Z catalyst. On further increase of the metal content to 8 wt%, a reduction in both LAS and BAS quantification was observed. This phenomenon could be a consequence of the inaccessibility of pyridine to some of these sites as result of the pore
blockage caused by the larger oxide particles. In any case, the total amount of acid sites increased in all modified samples compared with the parent zeolite.

The XRD patterns of the catalytic materials presented in Figure 2(b) confirmed the ZSM-11 structure for all the zeolites. In this way, it was possible to observe the characteristic signals at 2θ of 7–9° and 23–24° [19]. The diffraction pattern of NiO was also incorporated in this figure and the presence of its characteristic signals was emphasized. The intensity of these peaks increased when the amount of the metal incorporated augmented.

Results of reducibility of Ni species are presented in Figure 2c. All samples presented similar profiles, consisting mainly of a peak centered around 350 – 400 °C, while Ni(8)Z exhibited another broad peak at around 550 °C. The intensity and peak area of the Ni-zeolites spectra increased with Ni contents. The peak centered at lower temperatures corresponds to the highly dispersed Ni species, which have weak interactions with the support [20]. This peak can be attributed to the reduction of NiO to metallic nickel. It is noticeable that at higher metal content the signal became wider as consequence of diffusional limitations for bigger oxide particles. The second peak, centered at higher temperatures, can be assigned to Ni species with stronger interaction with the zeolite surface [18]. It is possible to infer that these species are also present in Ni(5)Z, but they are more prominent at higher metal content.

Figure 2d presents DRS UV–Vis spectra of the samples in order to verify the chemical environment of Ni present on them. As observed, the HZ spectrum presents a band at 200 nm that could be assigned to Al–O charge-transfer transition of four–coordinated framework Al, while the shoulder at 250 nm has been assigned to highly ordered structures with octahedral symmetry [21]. All Ni modified samples present the characteristic band of NiO
around 300 nm. In the case of Ni(8)Z there is a shift in this band to higher wavelength that may correspond to higher oxide particles [22], in accordance with XRD and TPR results. This observation confirmed the previous analysis made for the acid sites of the materials. Ni(8)Z, as consequence of the higher metal content presents the biggest oxide particles that blocks some pore’s mouths. Thus, internal acid sites became inaccessible. For this sample, bands at 390, 429 and 725 nm, characteristic of NiO, became more evident and their intensity increased as Ni content was higher.

Even when NiO is predominant in all the Ni-samples, there are also some absorption bands assigned to Ni\(^{2+}\) octahedrally coordinated (410, 650 and 740 nm) [23] indicating the coexistence of both species.

3.2. Catalytic activity

In order to determine Ni loading effect in ZSM-11 catalytic activity for biomass pyrolysis, a series of experiments were performed. Table 2 presents the mass balance of PS pyrolysis reactions catalyzed by the studied materials. As can be observed, biooil yields were similar in Ni(5)Z and Ni(8)Z catalyzed reactions. Nevertheless, a slight reduction in the biooil yield was verified when HZ and Ni(1)Z zeolites were employed. This result is a consequence of the increased selectivity towards permanent gases that occurs during the cracking of longer chain molecules.

With respect to biochar yield, it ranged around 29-30 wt%. These small variations were mainly caused by experimental error and the natural heterogeneity of PS. Considering the experimental set up, only pyrolysis vapors pass through the catalytic bed, so this observation could not be ascribed to a catalytic effect.
When analyzing coke yields, it was observed that the parent zeolite registered the highest coke deposition among the studied materials, suggesting that Ni incorporation to ZSM-11 zeolites prevents the formation of these carbonaceous products. This result is in agreement with Stanton et al. [24] who found that Ni-modified ZSM-5 zeolites generated lower coke deposits, compared with the unmodified fresh ZSM-5 catalyst. It is well known that coke deposits over catalysts can be generated by (1) polymerization of phenolic compounds (called thermal origin) and (2) transformation of oxygenated compounds over catalyst acid sites (called catalytic origin) [25]. Catalysts properties like porosity, particle size and surface area play an important role in coke formation [26].

### Table 2. Mass balance of PS pyrolysis reactions catalyzed with Ni-zeolites

|          | Biooil      | Biochar     | Gas         | Coke        |
|----------|-------------|-------------|-------------|-------------|
| Thermal  | 50.76 ± 2.54| 28.56 ± 1.43| 20.68 ± 1.03|             |
| HZ       | 47.81 ± 2.39| 27.54 ± 1.38| 17.42 ± 0.87| 7.23 ± 0.36 |
| Ni(1)Z   | 44.76 ± 2.24| 29.32 ± 1.47| 21.22 ± 1.06| 4.71 ± 0.24 |
| Ni(5)Z   | 49.97 ± 2.50| 30.33 ± 1.51| 15.28 ± 0.76| 4.44 ± 0.22 |
| Ni(8)Z   | 50.37 ± 2.52| 28.94 ± 1.45| 14.75 ± 0.74| 5.94 ± 0.30 |

### 3.3. Biooil upgrade

The effects of the Ni modified zeolites on the product distribution of PS pyrolysis is presented in Figure 3. Compounds found in the biooil were classified into oxygenated compounds (acids, aldehydes, ketones, phenols, alcohols, furans and esters) and hydrocarbons (aliphatics and aromatics). As can be observed, O-containing compounds were the main products in the thermal pyrolysis of PS. As expected, when Ni-zeolites were
employed, O-containing compounds decreased while hydrocarbons selectivity increased. Considering the reactor disposal, once the pyrolysis occurred, the vapors came in contact with the solid catalyst. Active sites are present on the surface and in the pores of the zeolites. When pyrolysis products make contact with them, reactions such as cracking, isomerization, aromatization and polymerization occurred. Thus, selectivity towards hydrocarbons increased. The main compounds identified were similar to those reported in literature [6] and they are listed in Table S1, in the Supporting Information file.

Biooils from all catalyzed reactions presented higher concentration of hydrocarbons than the thermal run. Ni(1)Z and Ni(8)Z catalysts presented lower hydrocarbons selectivity than the parent HZ zeolite. While, Ni(5)Z showed considerable deoxygenation and the highest hydrocarbons selectivity. This behavior suggests that there would be an optimal amount of metal to incorporate on a determined zeolite matrix. Kostyniuk et al. [18] found that zeolites with 5 wt% of Ni were the most active catalysts in hydrogenation, hydrocracking and isomerization reactions of biomass tar model compound mixture. It has been proposed that the impregnation of the catalyst with nickel significantly improved the selectivity towards hydrocarbons in the biooil from pyrolysis of lignocellulosic biomass [27]. The nickel particles strongly promote the hydrogen-transfer reactions that favor the formation of hydrocarbons during the catalytic improvement of the pyrolysis vapors [28].

It should be noted that the hydrocarbon fraction was mainly composed by aromatics (Figure 3b). It is well known that aromatization reactions require synergies of Brønsted and Lewis acid sites. Although BAS are active sites for aromatization reactions, dehydrogenation or hydrogen atom transfer reaction occurs on the LAS [29]. As presented in Table 1 Ni(5)Z
zeolite had the highest LAS and BAS. Consequently, lowest oxygenated compounds and highest aromatic selectivities were obtained over this material.

Figure 3c shows hydrocarbons distribution in the liquid products, according to the number of C-atoms per molecule. As can be observed, selectivity towards C10–C15 compounds was extremely low in the studied reactions.

On the contrary, Ni(5)Z favored the cracking to yield higher amounts of low molecular weight compounds, with 7–9 carbon atoms per molecule. This group includes valuable products like xylenes (C8), cumene and trimethylbenzene –TMB– (C9). Less valuable toluene (C7) was also present in the analyzed biooil. Nevertheless, the petrochemical industry can convert toluene to those important products by aromatic hydrocarbons transformations reactions. Xylene, a high demand compound in the chemical market, could also be produced through catalytic transalkylation of toluene with TMB [30].

Among O-containing compounds, two interesting compounds for the fine chemical industry were observed: furfural and 5-HMF (5-hydroxymethyl furfural). The former is mainly used as a selective solvent for the refining of lubricating oils and diesel fuels and as an intermediate chemical in the manufacturing of many solvents, plastics and agrochemicals. The latter can be converted to a variety of value-added furan compounds and can be used for the synthesis of polymers as it contains similar structure as aromatics. Synthesis of 5-HMF from biomass molecules, involves hydrolysis of the polymeric carbohydrates, isomerization of glucose into fructose and finally dehydration to 5-HMF [31].

Figure 4 shows the selectivity towards furans, furfural and 5-HMF. From the figure it is evident that 5-HMF was promoted by all catalysts since a complete absence of this
compound was observed in the thermal reaction. Approximately 50% of furans corresponded to furfural and 5-HMF. Similarly to hydrocarbons, Ni(5)Z was the most active catalyst in favoring the formation of 5-HMF. In the chemical pathway for cellulose transformation to 5-HMF, Brønsted acidity is believed to promote the depolymerization of oligosaccharides to monomeric anhydro-sugars [32]. The isomerization to fructose seems to occur in the presence of LAS and the dehydration is thought to be promoted by BAS [33].

3.4. Catalyst deactivation

Coke nature of spent catalysts was studied by FTIR spectroscopy (Figure 5a). An intense band at 3434 cm\(^{-1}\) could be observed in all samples. That band is attributed to bridging hydroxyl groups, while the smaller band at 3234 cm\(^{-1}\) is attributed to H-bonding between acidic hydroxyl groups and adsorbed molecules. The bands between 2800–3000 cm\(^{-1}\) are attributed to the CH stretching modes (symmetric and asymmetric) of CH\(_3\) groups. The bands from 1300–1700 cm\(^{-1}\) can be assigned to the CH bending of paraffinic groups and the CC stretching modes of unsaturated groups. The bands around 1450 – 1700 cm\(^{-1}\) are mainly attributed to aromatics structure vibration [34]. Figure 5b shows FTIR spectroscopy of fresh HZ where a total absence of carbon signals was observed.

Catalyst stability was evaluated with six consecutive reaction cycles. Since products yields (biooil, biochar and gases) did not suffer significant variations, six main compounds, including furans and aromatics, were chosen to test the zeolite deactivation. The most active catalyst -Ni(5)Z- was selected and its re-uses are presented in Figure 6. Results showed partially deactivation just in the second cycle. This behavior can be explained by coke
deposition. From Table 1, it could be observed how $S_{\text{BET}}$ decreased in all spent catalysts. In the case of Ni(5)Z, an area loss of about 100 m$^2$ g$^{-1}$ was obtained after the first use.

From Figure 6 it is possible to confirm an increment on furfural selectivity as reuses cycles advanced. However, the other compounds analyzed were reduced (Selectivities < 1 wt%). This behavior could be explained by the surface area reduction previously commented. When zeolites pores were physically blocked by coke deposition, pyrolysis products could not get in contact with the catalyst active sites. Thus, reaction products resulted to be quiet similar to non-catalytic reactions. Besides, Renzini et al. [19] found that coke deposition over ZMS-11 zeolites caused a decrease of both BAS and LAS.

However, it is noteworthy that upon deactivation Ni(5)Z could be easily regenerated by calcination. After that, catalytic activity was completely recovered. Figure S1 presents XRD pattern of the regenerated catalyst, confirming ZSM-11 structure and crystallinity. Coke deposition resulted in a temporarily catalyst poisoning and acid sites blockage that could be thermally solved.

### 3.5. Activated biochars characterization

Table 3 presents physicochemical characteristics of the synthetized AB samples. Biochar is presented for comparison reasons. As can be observed, $S_{\text{BET}}$ doubled when the KOH:biochar ratio increased from 1:1 to 3:1. In general, BET surface area increases when KOH content or temperature increase [12,35]

Proximate analysis revealed that fixed carbon in the activated biochars was higher than in the starting biomass, which resulted from an effective carbonization process [36]. As the temperature increases, it is expected that the carbon content increases and that of the volatiles
decreases, since devolatilization processes predominantly occur [37]. From the analysis of activated materials, it could be observed that the fixed carbon content decreased as the surface area increased, thus registering AB 3:1 sample the lowest fixed carbon value. Moisture content in this sample was almost 4% higher, suggesting that it is slightly more hygroscopic than AB 1:1.

Table 3. Physicochemical characteristics of activated biochars.

|                | Proximate analysis (%w/w) | S\text{BET} (m^2 g\text{-1}) |
|----------------|---------------------------|-------------------------------|
|                | Moisture | Volatile matter | Fix carbon | Ash  |                     |
| Biochar        | 6.83     | 27.95           | 58.69      | 6.53 | 215                  |
| AB 1:1         | 20.11    | 10.97           | 64.45      | 4.47 | 832                  |
| AB 3:1         | 23.89    | 12.6            | 58.51      | 5    | 1645                 |

\textsuperscript{a} Determined by TGA.

XRD diffractograms and Raman spectra display the crystallographic structures of the activated materials (Figure 7). All specimens presented a broad band located at 2\theta = 20-30\degree which is characteristic of amorphous materials, suggesting the existence of amorphous carbon caused by incomplete carbonization [38]. The peak at 2\theta = 23.5\degree corresponds to the (002) graphite planes. From Figure 7a it can be observed that this broad peak is stronger in biochar and weaker in the AB samples, proving an increase in the degree of graphitization. Figure 7b presents Raman spectra of the as-prepared porous carbon materials. The D-bands (~1356 cm\textsuperscript{-1}) and G-bands (~1604 cm\textsuperscript{-1}) correspond to the disordered carbon and graphite carbon, respectively [39]. D and G bands ratio (I_D/I_G) changed from 0.959 in pyrolysis
biochar to 0.999 in AB 3:1 sample, indicating a higher graphitization degree at a higher
temperature.

The FTIR spectra of the AB samples are shown in Figure 8. The presence of surface
functional groups is considered an important factor that determines the adsorption behavior
of activated carbons. The vibrations of some functional groups could be observed. The band
at 400-750 cm\(^{-1}\) was assigned to the stretching vibration of C-C and the one at 750-900 cm\(^{-1}\)
was responsible for the bending of C-H. The signals at 1050 cm\(^{-1}\) and 1250 cm\(^{-1}\) were
attributed to the vibrations of C-O and C-O-C and the peak at 1480 cm\(^{-1}\) would indicate the
stretching vibration C=C [35]. The signal at 1700 cm\(^{-1}\) was assigned to the C=O stretch and
the one at 1750 cm\(^{-1}\) resulted from the presence of -COOH groups. While the band at 2800-
2900 cm\(^{-1}\) was responsible for the stretching of aliphatic CH, the broad band at 3400 cm\(^{-1}\)
was assigned to the vibration of –OH, corresponding to adsorbed water molecules [35,40].

SEM micrographs of the as-prepared materials are presented in Figure 9. AB 1:1
sample presented a rib-like structure (Fig. 9a) on which the presence of numerous dispersed
pores could be observed. As the KOH content increased, the precursor (biochar) continued
decomposing, and the formation of many new macropores could be observed in AB 3:1
sample (Fig. 9b). Thus indicating that the ribs observed in AB 1:1 were transformed into
channels in AB 3:1. Consequently, the opening of the macropores possibly contributed to the
formation of new micro and mesopores on the internal surfaces.

4. Conclusions

With aims for a circular bioeconomy, the valorization and recycling of PS in two
subsequent product systems was studied. The first system consisted of catalytic fast pyrolysis
of the residual biomass where a group of Ni-ZSM-11 matrices was tested. When varying Ni content, a surface area reduction was obtained, but acid sites were improved. From the evaluated materials, Ni(5)Z showed the best results in terms of hydrocarbons and platform molecules selectivities. This catalyst was further measured in terms of stability over several reaction cycles. The temporary poisoning was easily solved by calcination, after which the material recovered its pristine crystallinity and catalytic behavior. Thus, it is possible to affirm that nickel ZSM-11 zeolites with a 5 wt% of loading are ideal catalysts for the pyrolytic conversion of peanut shell to interesting platform molecules.

The second system consisted of synthetizing AB employing the residual biochar from the previous pyrolysis as the precursor. The materials were produced by a simple thermo-chemical procedure, employing KOH as activation agent. Surface area ($S_{\text{BET}}$) could be significantly increased upon activation, from 215 m$^2$/g in biochar to 1645 m$^2$/g when KOH:biochar ratio was 3:1. Considering the type and quantity of surface functional groups found on these materials, they could be used for a variety of sorption processes.

These results proved to be an example of an efficient biobased renewable resource management.

**Associated content**

- File name: Fermanelli et al. – Supporting Information. File format: .docx.
- Data: XRD pattern of regenerated Ni(5)Z. Main compounds detected in bio-oils by CG-MS analysis.
Availability of data and materials

All data generated or analyzed during this study are available from the corresponding author, upon reasonable request. The necessary data that were generated and analyzed during the study are included in this published article.

Competing interests

The authors declare they have no competing interest.

Author Contributions

Carla S. Fermanelli: investigation, methodology, data curation, writing – original draft. Adrián Chiappori: resources. Liliana Pierella: project administration. Clara Saux: conceptualization, writing – review and editing, supervision. All authors have given approval to the final version of the manuscript.

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Figure legends

**Figure 1.** Schematic illustration of open-loop recycling between three systems. Adapted from Olofsson and Börjesson [8].

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