

Article

Hydrothermal Valorization via Liquid Hot Water and Hydrothermal Carbonization of Pea Pod Waste: Characterization of the Biochar and Quantification of Platform Molecules

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Featured Application: obtention of biofuels and platform molecules from agricultural waste.

Abstract: Pea pod cultivation spans various regions and climates, with a global production of around 20 million tons. The pea peel wastes, which make up 30–40% of the total weight of the peas, are freely available in large quantities. The biomass used was characterized via ultimate, proximate, and structural analysis, obtaining 20.2%w of cellulose and 17.4%w of hemicellulose, which, via valorization processes, can be transformed into platform chemicals. Hydrothermal valorization presents itself as a clean form of treatment for these wastes, ranging from 120 to 180 °C (LHW) and from 180 to 260 °C (HTC). The use of LHW can lead to the production of sugars (up to 70%w yield) and levulinic acid (4%w yield), while the use of HTC leads to formic acid (40%w yield) and levulinic acid (4%w yield). The use of LHW for longer periods favors the production of HMF and furfural. The use of homogeneous catalysts (H₂SO₄, CH₃COOH, KOH, and NaHCO₃) was implemented, and their selectivity was described. Solid fractions of LHW and HTC were characterized via FTIR and elemental analysis, and the change in their structure was described as they shifted from biomass to biochar. Optimal conditions for each platform chemical were reported to best utilize the pea pod waste.

Keywords: pea pods; hydrothermal valorization; platform chemicals; catalysts; HTC; LHW

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1. Introduction

Thermochemical processes such as combustion, pyrolysis, torrefaction, gasification, liquid hot water extraction (LHW), hydrothermal carbonization (HTC), liquefaction (HTL), or gasification (HTG) are some of the most common methods used to chemically transform biomass into energy and chemical products by using heat in biorefineries [1]. Among all thermochemical processes, HTC has gained considerable attention due to its inherent advantages, such as the use of water as a reaction medium, which explains why there is no need to dry the biomass at the beginning of processing, reaction times in the range of 5 min to several hours, lower reaction temperatures (in the range 180–280 °C) compared to other thermochemical processes, which also means that it is a safer process to conduct experimentally, and the high yield of carbonaceous solids [2].

HTC, also known as hydrous pyrolysis, is carried out by heating a mixture of biomass with a specific ratio of water under subcritical conditions to potentially make a practical variety of products such as hydrochar, high carbon content products, value-added products that vary between platform chemicals, fuels, carbon nanospheres, low-cost adsorbents, and soil amenders [3,4]. This process has not been commercialized yet because several challenges must be overcome, pointing to the main challenge, which is the development of a feeding system that feeds the mixture of biomass with water against the high pressure of the reactor. The most common biomasses used for HTC processes are the organic fraction

of municipal solid waste (MSW), sewage sludge, agro-industrial waste, and nontraditional feedstock sources such as wet animal manures, human waste, and sewage sludges, in addition to aquaculture and algal residues [4,5].

The HTC process is commonly used as a pretreatment stage integrated with other thermochemical processes, which, in continuous operation, would promote the development of biorefineries [1]. Biorefinery is defined as the facility, plant, or cluster of facilities that integrates sustainable biomass conversion processes to produce value-added marketable products like food, feed, materials, chemicals, and energy such as fuels, power, or heat [6,7]. The technological process in biorefinery aims to jointly apply thermochemical, biochemical, mechanical/physical, and chemical processes to depolymerize and deoxygenate the biomass components, in this case, the pea pod waste, so value-added products are made by a biorefinery approach [8].

Liquid hot water pretreatment, also known as autohydrolysis, is a method used to improve the enzymatic hydrolysis of biomass, leading to the production of free sugars. This process involves treating the biomass with hot water at elevated pressures, which helps to break down the hemicellulose and reduce the recalcitrance of the material. The use of liquid hot water pretreatment for various types of biomasses, including sugarcane bagasse, poplar, and Italian green pepper waste, has been studied to valorize these materials for the production of biofuels and other value-added chemicals [9,10]. The effectiveness of this pretreatment method has been attributed to its ability to enhance the saccharification of polysaccharides, particularly cellulose, into glucose, making it a promising approach for the efficient utilization of biomass resources [10].

Agro-industrial biomass utilization has gained significant attention in recent years due to its potential to reduce reliance on fossil fuels and address waste management challenges. Biomass, derived from agricultural and industrial processes, is a widely available resource that can be used for various energy needs, such as electricity generation, industrial process heat, and residential heating [11]. The energy potential of biomass in the South Asian Association for Cooperation (SAC) countries is more than 8 billion gigajoules, with potential biogas energy capacity ranging from 51 MW to over 200 MW [12]. Biomass residues from various industries, such as coconut, rice, palm oil, wood, and sugar, contribute to the biomass potential in the SAC countries, with a total capacity of 380,000 MW [12]. Sugar cane biomass has a potential capacity of 15,751 MW in the SAC countries, while forest biomass has a potential capacity of 929 Mm³ of stock annually. These statistics highlight the potential of agro-industrial biomass utilization as a sustainable and renewable energy resource. However, further research and development are needed to optimize the production, transportation, and utilization of biomass to fully realize its potential in the energy landscape [13].

Pea pod production plays a crucial role worldwide, supplying a significant portion of the global vegetable market and contributing to the sustenance of millions of people. Peas are one of the most cultivated legumes, renowned for their nutritional value, sweet flavor, and versatility in culinary applications. Pea pod cultivation spans various regions and climates, making them accessible to both developed and developing countries, with a global production of around 20 million tons [10]. Peas are rich in essential vitamins, minerals, and dietary fiber, promoting good health and supporting balanced diets [14]. On the other hand, pea waste produced in large quantities during industrial processing has a negative impact on the environment and can release hazardous gases [15]. The pea peel wastes, which make up 30–40% of the total weight of the peas, are freely available in large quantities [15]. Consequently, a variety of techniques are needed to transform these wastes into valuable goods with high nutritional value. Pea pod waste has been used for cellulolytic enzyme production as well as a feed for goat bucks [16], ruminants [17], and as a source of dietary fiber [18,19]. From a hydrothermal point of view, the valorization of pea pods has been researched, obtaining monosaccharides and polysaccharides [20], polyphenols [21,22], and hydrochar [23].

The scope of this paper is to analyze the different processes that take place in the hydrothermal valorization of pea pods by modifying variables such as time, temperature, and catalysts, and finally describe the behavior of the biomass by adjusting it to a kinetic model and focusing on the byproducts of the best economic and energetic valorization.

2. Materials and Methods

2.1. Characterization

2.1.1. Proximate Analysis

The essays consisted of moisture, ash, volatile matter, and fixed carbon, and the procedure is shown in the Supplementary Materials.

2.1.2. Ultimate Analysis (C H O N Analysis)

Report NREL/TP-510-42620 was used as a guide alongside a Thermo Scientific FLASH 2000 Series Organic Elemental Analyzer.

2.1.3. Structural Analysis (Lignin, Hemicellulose, and Cellulose)

The process used is reported in the procedure for methods for dietary fiber, neutral detergent fiber, and nonstarch polysaccharides in relation to animal nutrition. The fiber in neutral detergent, the fiber in acid detergent, and the fiber in lignin were measured.

2.2. Hydrothermal Essays

2.2.1. Liquid Hot Water (Temperatures from 120 to 180 °C)

A 100 mL batch reactor consisting of a reactor jacket made of Teflon inside the stainless steel reactor (Supplementary Materials) was set to different temperatures (ranging from 120 °C to 180 °C) and times (1–5 h) with 3 g of pea pods and 27 g of water. The heating was performed by inserting the reactor in an oven set to LHW temperatures, and the heating time was measured when the expected temperature was reached. Autogenous pressure was generated. Then, the reactor was cooled, and the samples were filtered in order to separate the liquid and solid phases. The solid phase was washed and later analyzed via elemental analysis and infrared spectroscopy. The pH and conductivity of the liquid phase were measured as a preliminary follow-up. Finally, the liquid samples were sent to an HPLC-RI (High-Performance Liquid Chromatography with Refractive Index Detection) for the identification and quantification of the present chemical species.

The set of experiments is presented in Table 1.

Table 1. Set of experiments in the LHW range.

Experiment	Time (h)	Temperature (°C)
1	1	120 ± 0.1
2	1	130 ± 0.1
3	1	140 ± 0.1
4	1	150 ± 0.1
5	1	160 ± 0.1
6	1	170 ± 0.1
7	1	180 ± 0.1
8	2	180 ± 0.1
9	3	180 ± 0.1
10	4	180 ± 0.1
11	5	180 ± 0.1

2.2.2. Hydrothermal Carbonization (180–260 °C)

A 500 mL stainless steel batch reactor (Supplementary Materials) was set to different temperatures (ranging from 180 to 260 °C) and times (1–5 h) with 10 g of pea pods and 90 g of water (Table 2). The heating was performed by programming the heating of the reactor jacket heating resistance to a certain HTC temperature. The heating time was measured

as soon as the expected temperature was reached. Autogenous pressure was generated. Then, the reactor was cooled, and the samples were filtered to separate the liquid and solid phases, and they were characterized as previously performed in LHW.

Table 2. Set of experiments in the HTC range.

Experiment	Time (h)	Temperature (°C)
1	1	200 ± 2
2	1	220 ± 2
3	1	240 ± 2
4	1	260 ± 2
5	2	200 ± 2
6	3	200 ± 2
7	4	200 ± 2
8	5	200 ± 2

2.3. Analysis of the Solid Phase

2.3.1. Infrared Spectroscopy (ATR)

The solid phase was cleaned with water, ethanol, and acetone, dried at 115 °C for 30 min, and analyzed by ATR on a Nicolet iS10 spectrometer by Thermo Fisher Scientific (Waltham, MA, USA).

2.3.2. Elemental Analysis

The same process implemented for the ultimate assay of the biomass was used for all the solid phases produced in each hydrothermal essay.

2.4. HPLC Quantification and Characterization

The HPLC-RI method development and optimization involve a series of experiments to optimize parameters such as column choice, mobile phase composition, flow rate, and temperature. Validation ensures accuracy, precision, specificity, and robustness by testing the method's performance using appropriate standards and samples. The final method consisted of a mobile phase of 0.005 M H₂SO₄, a flow rate of 0.5 mL/min, and a Shodex SH1821 column set in a 60 °C oven. It can be a valuable tool for the separation and quantification of compounds in various applications, providing reliable and accurate analytical results. A Hitachi Elite LaChrom chromatograph coupled to a Hitachi L-2490 refractive index detector at 40 °C was used. In this case, the idea is to separate the most expected by-products in the valorization of cellulosic and hemicellulosic biomass. These include glucose and xylose, highly polar monosaccharide sugars (with six and five carbon atoms, respectively), a simple organic acid, levulinic acid, HMF (5-Hydroxymethylfurfural), and furfural. Glucose and xylose are polar sugars that elute early in the chromatogram. Formic acid and levulinic acid are polar acids that elute later. HMF, which is less polar than acids but more polar than furfural, elutes next, and furfural, the least polar, elutes last. These compounds have distinct chemical properties, making HPLC an excellent choice for their separation. In Figure 1, the separation of the standards is shown. Sugars are not completely separated, so the reports given in this research will be given as "sugars", not individually. Table 3 shows the retention times of the standards.

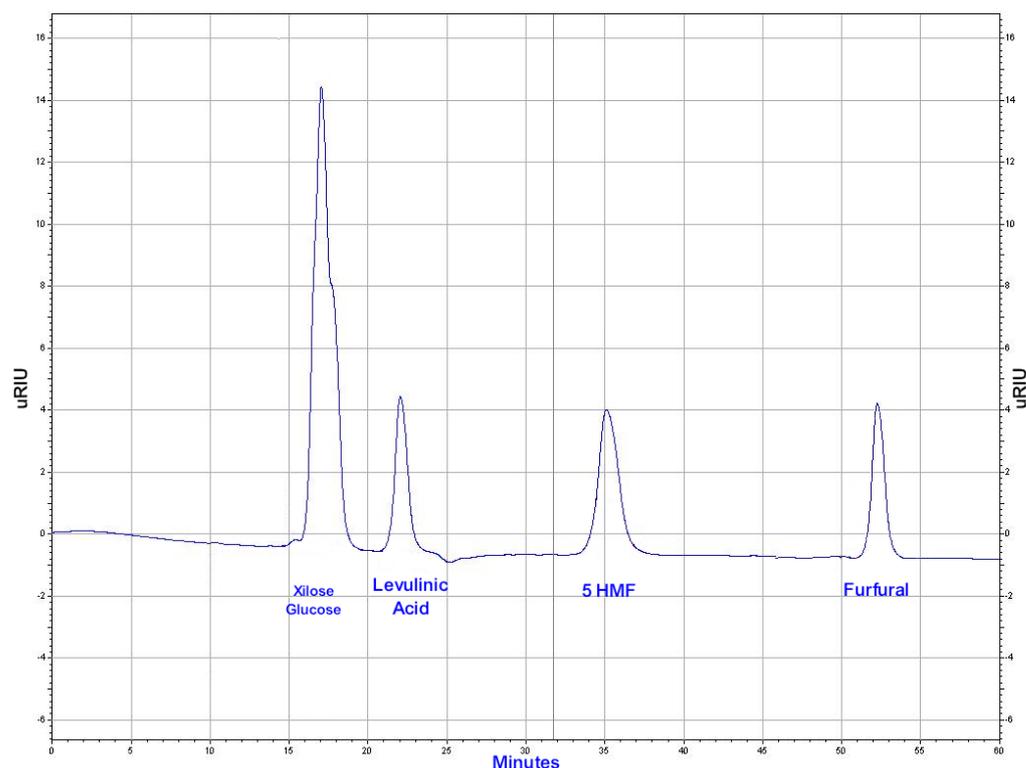


Figure 1. Chromatographic design for platform chemicals (PC).

Table 3. Retention time for separation of standards of PC.

Standard	Retention Time (min)
Glucose	16.7971
Xylose	17.1698
Formic acid	20.6158
Levulinic acid	22.3054
HMF	35.2803
Furfural	51.3499

2.5. Condition Optimization

2.5.1. Use of Catalysts

In order to optimize the operation conditions, the implementation of homogeneous catalysts was suggested. Homogeneous acid and basic catalysts play a significant role in the hydrothermal valorization of biomass. In the hydrothermal liquefaction process, inorganic acid catalysts such as H_2SO_4 are extensively applied to facilitate the conversion of biomass into valuable products, including aviation fuel precursors [24]. Additionally, homogeneous basic catalysts, such as carbonates and hydroxides of alkali metals, have been studied for their role in the valorization of biomass feedstocks, including red macroalgae and livestock manure, to enhance biocrude oil and hydrochar production [25,26]. These catalysts promote the depolymerization and upgrading of biomass components under hydrothermal conditions, offering a sustainable approach to converting biomass into biofuels and chemicals [27]. In this research, solutions of H_2SO_4 0.02 M, CH_3COOH 0.2 M, KOH 0.02 M, and NaHCO_3 0.2 M were prepared and used instead of water in the biomass/water ratio of 1:9 (3 g of biomass and 7 g of catalyst solution) to improve the yield and selectivity of the biomass conversion.

2.5.2. Optimization Based on Platform Chemicals

After quantifying the platform chemicals in different hydrothermal ranges and times and using catalysts, a report of the conditions that produce an increase in the yield of each PC is given.

2.6. Kinetic Overview of Hydrolysis in LHW

A preliminary analysis of the kinetics of the lignocellulosic biomass hydrolysis to sugars is presented via mathematical and graphical treatment of the data in order to determine the order of the reaction of each of the hydrothermal processes.

3. Results

3.1. Characterization of the Biomass

3.1.1. Proximate Analysis

The proximal assay shows the initial characteristics of the biomass (Table 4). Understanding the composition of biomass, including moisture content, ashes, volatile matter, and fixed carbon, is crucial for its valorization, particularly in hydrothermal processes [28]. These components play a significant role in the formation of thermal products and the overall efficiency of the process. The presence of moisture in biomass affects the hydrothermal liquefaction process. Moisture content influences the heat capacity, thermal conductivity, and swelling behavior of biomass, which in turn affects the efficiency of the process and the properties of the final products [29]. Ashes are inorganic residues formed from the mineral components of biomass, such as Ca, K, Si, Mg, Al, S, Fe, P, Cl, and Na, as well as some trace elements like Mn and Ti [29]. The ash content in biomass can vary from less than 1%w for wood to as much as 12%w for straw and bagasse (sugar cane residue) [30]. The presence of ash affects the corrosiveness of the reaction mixture and the overall efficiency of the process. Volatile matter refers to the fraction of biomass that evaporates during the hydrothermal process. This fraction includes light and heavy compounds that may contribute to the formation of thermal products or be responsible for undesired reactions [30]. The composition of volatile matter can influence the yield and quality of the final products. Fixed carbon is the fraction of biomass that remains after the hydrothermal process. It consists of carbon-rich compounds, such as char, which can contribute to the formation of bio-oil or other value-added products [30]. The fixed carbon content can affect the efficiency of the process and the properties of the final products. By understanding the composition of biomass and optimizing the hydrothermal process conditions, it is possible to maximize the yield of valuable products, such as bio-oil, chemical platforms, or biochar, while minimizing the formation of undesired compounds.

Table 4. Proximate analysis of the pea pod waste sample.

Essay	Result (%w) ¹	Result (%w) ²
Moisture	7.77 ± 0.6	7.0
Ashes	4.22 ± 0.11	3.5
Volatile matter	74.18 ± 0.11	78.0
Fixed carbon	13.0	18.0

¹ Results obtained in the present paper; ² Results reported for pea pods [28].

The two sets of results show some differences in the volatile matter and fixed carbon content, with the second set of results showing higher values for both. The ash content is also slightly lower in the second set of results. The moisture content is similar in both sets of results. These differences in composition could impact the yield and quality of thermal products obtained from the hydrothermal valorization of pea pods and are caused by changes in the production of the pea pods, such as weather, soil, and crop variety [31]. Understanding the composition of biomass is crucial for optimizing the valorization process and developing value-added products from biomass.

3.1.2. Ultimate Analysis

The ultimate analysis of the pea pod waste is presented in Table 5. With these results, the O/C, H/C, and C:N ratios are obtained. The O/C, H/C, and C:N ratios are important parameters in the characterization of organic compounds, including biomass and coal. The H/C ratio is a measure of the degree of saturation of a compound, with higher values indicating greater saturation. The O/C ratio reflects the oxygen content relative to carbon, and the N/C ratio indicates the nitrogen content relative to carbon. These ratios are commonly used in the van Krevelen diagram (Figure 2), which is a graphical representation of the O/C versus H/C ratios of organic compounds [32]. This diagram is useful for classifying and comparing the composition of organic matter, including biomass and coal, and for understanding their origin and evolution. For example, in the case of coal, the H/C ratio shows a sharp decline in bituminous coals and anthracites, reflecting increased aromatization of the lignin structure during coalification. In the context of biomass, the O/C ratio is of great importance, as a high O/C ratio results in a low bulk energy density, highlighting the need to lower the oxygen content for efficient energy conversion [33]. Therefore, these ratios are crucial for understanding the properties and behavior of organic compounds and for optimizing their utilization in various applications.

Table 5. Ultimate analysis of pea pods.

Element	Result (%w) ¹	Result (%w) ²
Carbon	43.3	39.32
Hydrogen	5.95	4.75
Oxygen	49.02	53.3
Nitrogen	1.71	2.40
Sulfur	0	0.23
O/C ratio	0.85	1.02
H/C ratio	1.65	1.45
C/N ratio	29.65	19.11

¹ Results obtained in the present paper; ² Results reported for pea pods [28].

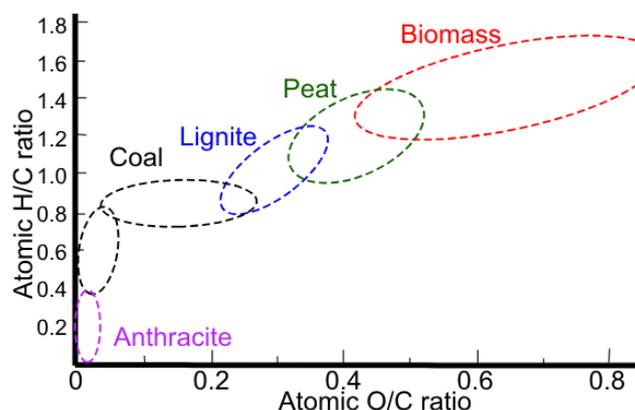


Figure 2. Van Krevelen diagram and characterization of pea pod waste.

Figure 2 shows the characterization of the pea pod waste as biomass, and its C/N ratio shows that it is appropriate to be used for processes of transformation using microorganisms due to the ratio being higher than 24, the ideal microbial diet, and making it have a slower relative decomposition rate. When comparing the results to those found in previous papers, the biggest difference is the lower C/N ratio in previous research and the higher O/C ratio, both due to the nature of the pea pod.

3.1.3. Structural Analysis

Table 6 presents the percentages obtained for hemicellulose, cellulose, and lignin, which are the main structures that will be later hydrolyzed into sugars and other platform

chemicals (PC). In both the quantification performed in this paper and the one from other researchers, hemicellulose and cellulose have a similar ratio, with cellulose being the most significant one. On the other hand, the amount of lignin is low, which is a positive aspect of producing sugar since lignin is known to be an inhibitor of the sugar hydrolysis of hemicellulose and cellulose [34]. The presence of lignin in biomass can strongly interfere with the yields of sugars and furans produced from raw materials, while delignified biomass provides a significant improvement in product yields. Knowing the principal lignocellulosic structures present in the pea pod waste, it is expected that valorization products from hemicellulose and cellulose will be obtained, such as HMF, furfural, levulinic acid, sugars, and formic acid.

Table 6. Structural analysis of pea pods on a dry basis.

Essay	Result (%w) ¹	Result (%w) ²
Hemicellulose	17.4 ± 0.5	41.0
Lignin	5.0 ± 0.3	3.0
Cellulose	20.2 ± 0.1	45.0

¹ Results obtained in the present paper; ² Results reported for pea pods [28].

3.2. Valorization via Liquid Hot Water (Temperatures from 120 to 180 °C)

Preliminarily, the acid and sugar production in the liquid phase was monitored with pH and conductivity measurements in reactions performed for 1 h at different temperatures in the LHW range. Figure 3 shows the results obtained. Higher temperatures resulted in greater pH values, which, in addition to higher conductivity measurements, were correlated to acid production but without a major change in its production.

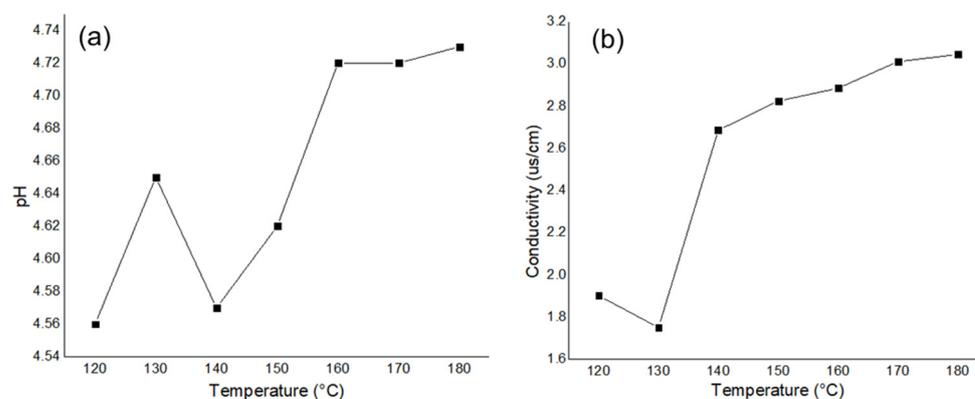


Figure 3. Preliminary follow-up of the content of platform chemicals in reactions for 1 h from 120 to 180 °C by (a) pH vs temperature and (b) conductivity vs temperature.

Then, the reaction time was varied at a temperature of 180 °C to see if it was a crucial factor to consider. The results are shown in Figure 4. The conductivity measurements, which revealed more ions in the liquid phase at longer reaction periods, were consistent with the pH measurements, which showed that higher reaction times produced more acids than lower reaction times. Conversely, a reaction time of 1 h produced the maximum amount of sugars, as they are species that do not contribute to lowering the pH or the amount of ions in the solution.

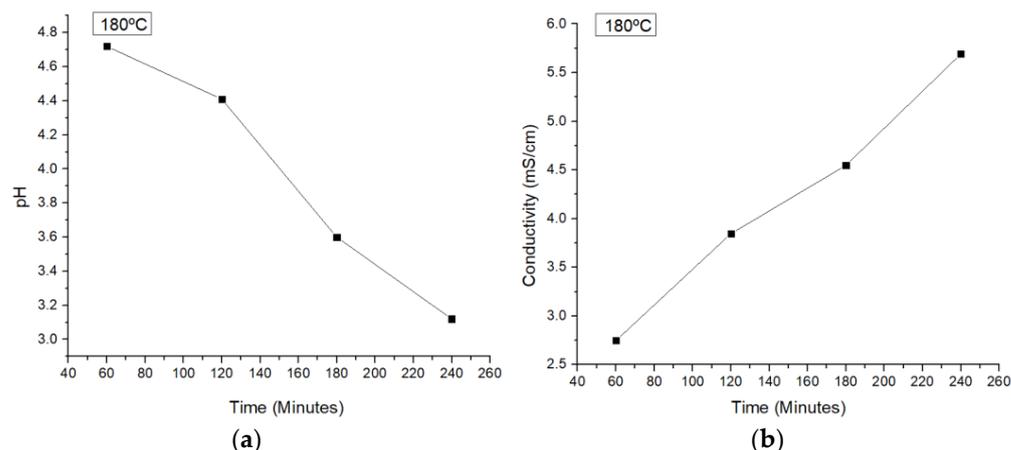


Figure 4. Preliminary follow-up of content of platform chemicals at 180 °C for 1–4 h. (a) pH vs time (b) Conductivity vs time.

3.2.1. Quantification of Liquid Fractions

The liquid phase analysis and quantification of the corresponding components were carried out with an HPLC-RI. As shown in Table 7 and Figure 5, the sugar yield varied between 36.9% and 70.0%w when reactions of 1 h at 120 °C and 180 °C were performed, respectively, showing that the more energy provided via heat to the system, the higher the hydrolysis of the lignocellulosic structures. Moreover, levulinic acid production was achieved only at the higher reaction temperatures, 170 °C and 180 °C. There was not enough energy in the system to achieve the transformation of sugars into other molecules, which, as will be seen later, can be achieved by longer reaction times, higher temperatures, or the use of catalysts.

Table 7. Quantification of platform chemicals via LHW at 1 h.

Temperature (°C)	Time (h)	Concentration PC (g/L)		Yield * (%w)
		Sugars	Levulinic Acid	
120	1	18.098		36.903
130	1	18.258		37.228
140	1	18.445		37.610
150	1	23.594		56.265
160	1	26.004		53.023
170	1	30.450	0.336	62.089
180	1	34.818	0.577	70.001

* Based on lignocellulosic structure.

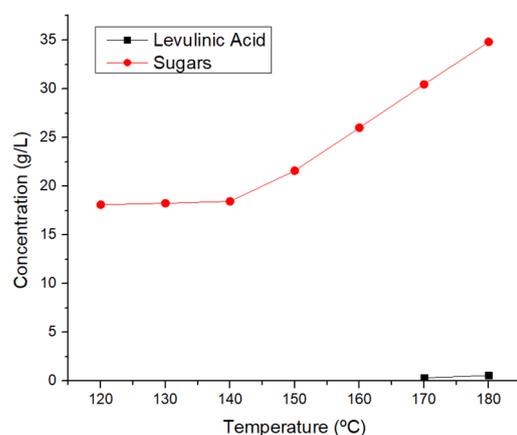


Figure 5. Obtention of platform chemicals via LHW for 1 h.

Figure 6 and Table 8 show that PC are obtained by the reaction of sugars from the lignocellulosic biomass, previously broken, and subsequent dehydration reactions of the sugars. The dehydration reactions, in the first place, can lead to products such as HMF or furfural, depending on whether the sugar that underwent dehydration was glucose or xylose, respectively. The subsequent dehydration reactions lead to products such as levulinic acid and formic acid.

Table 8. Quantification and yields of platform chemicals via LHW (180 °C) for 1–4 h.

T (°C)	Time (h)	Concentration PC (g/L)					Yield (%w) *
		Sugars	Levulinic Acid	Formic Acid	HMF	Furfural	
180	1	34.818	0.577				70.001
180	2	26.341	1.063	2.392	0.299		62.284
180	3	15.539	1.120	4.067	0.757	0.632	51.528
180	4	1.250	1.244	8.566	1.032	1.249	42.838

* Based on lignocellulosic structure.

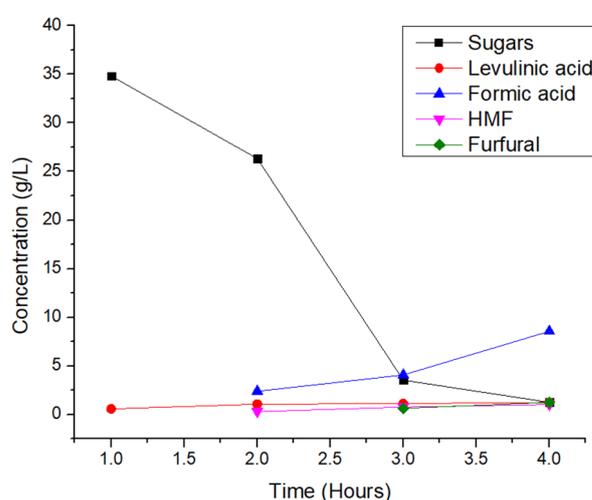


Figure 6. Obtention of platform chemicals via LHW (180 °C) for 1–4 h.

3.2.2. Kinetics of Hydrolysis

A preliminary overview of the kinetics of the hydrolysis of the lignocellulosic biomass into sugars is presented in the Supplementary Materials, where the concentration of sugars vs. the time of reaction is graphed as well as some mathematical transformation to propose a pseudo-order of the reaction. In this, it can be seen that the transformation that best assimilates to a line is that of Order 1, which is a common model used to describe the enzymatic hydrolysis of lignocellulosic biomass into sugars. Studies have shown that this model accurately describes the hydrolysis of various biomasses under different pretreatment conditions, indicating that the hydrolysis reaction appears to follow first-order kinetics. For example, the hydrolysis of cellulose and the formation of glucose decomposition products catalyzed by formic acid, as well as the acid-catalyzed hydrolysis of cellobiose in an ionic liquid, have been shown to follow pseudo-first-order kinetics.

3.2.3. Characterization of Solid Fractions

Infrared Spectroscopy of LHW solid fractions On the other hand, the solid fraction was analyzed with FTIR spectroscopy. Figure 7 shows the comparison of the spectra acquired after 1 h of reaction time at 120 °C. At temperatures of 160 °C and 180 °C, the biomass remains unreacted. The absorption bands correspond to functional groups of O-H (3284–3308 cm^{-1}), C-H stretching of aliphatic groups (2919–2923 and 2853 cm^{-1}), C=O (1705 cm^{-1}), C=C of aromatic compounds (1608–1622 and 1516 cm^{-1}), and C-O-C,

C-O-H, and C-O vibrations predominantly of groups present in cellulose, hemicellulose, and lignin ($1500\text{--}1350$ and $1300\text{--}1150\text{ cm}^{-1}$). The differences in band absorption are related to concentration.

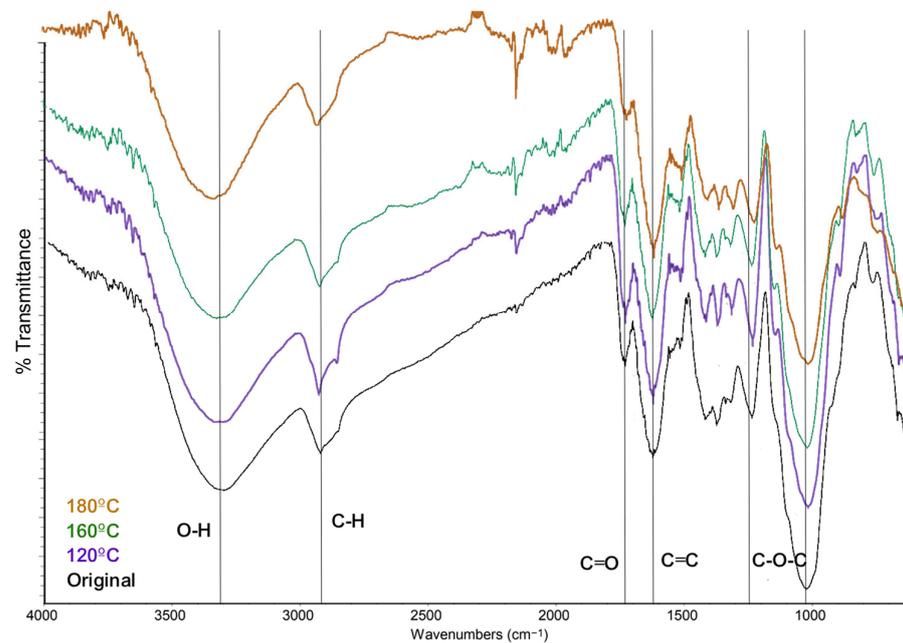


Figure 7. Infrared spectrum of LHW for 1 h.

Moreover, the solid phase of the reaction at $180\text{ }^{\circ}\text{C}$ at different reaction times was analyzed, and the results are shown in Figure 8. It shows that longer reaction times can decrease the transmittance of the band associated with cellulose, hemicellulose, and lignin ($1000\text{--}1500\text{ cm}^{-1}$), confirming that at higher reaction times, those structures are broken in order to form sugars.

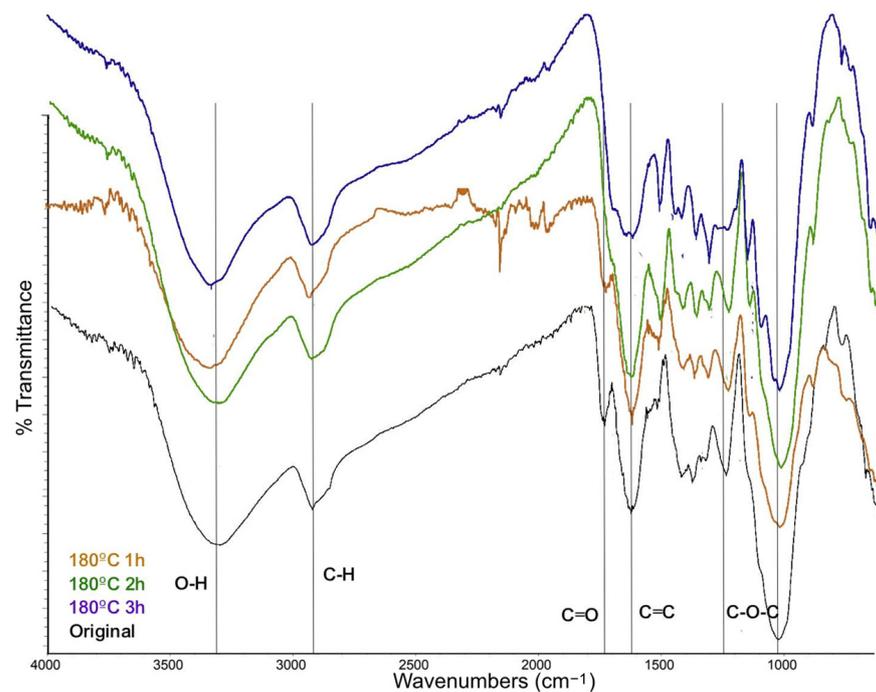


Figure 8. Infrared spectrum of LHW at $180\text{ }^{\circ}\text{C}$ for 1–3 h.

Elemental Analysis of LHW Solid Fractions

In order to track the changes in the elemental composition of the biomass, the elemental analysis of the solid fractions obtained via LHW is presented in Table 9. It can be seen that there is not a significant change in the O/C and H/C ratios because the biochar obtained still has the characteristics of biomass (Figure 9); hence, it does not assimilate to the properties of coal. The biggest change takes place at 170 °C, where the amount of carbon increases, influencing the ratios of characterization.

Table 9. Elemental analysis of solid fractions of LHW.

T (°C)	Time (H)	%C	%H	%N	%O	O/C	H/C	C:N
Original	Original	43.33	5.95	1.71	49.02	0.85	1.65	29.65
120	1	45.99	6.22	1.13	46.67	0.76	1.62	47.67
130	1	45.62	6.01	0.97	47.40	0.78	1.58	55.14
140	1	47.82	5.82	2.20	44.16	0.69	1.46	25.39
150	1	51.13	5.76	1.38	41.74	0.61	1.35	43.32
160	1	45.88	5.94	1.16	47.02	0.77	1.55	46.16
170	1	53.71	6.08	1.69	38.52	0.54	1.36	37.09
180	1	44.79	5.77	1.48	47.96	0.80	1.55	35.43
180	2	43.33	5.58	0.88	50.20	0.87	1.55	57.41
180	3	49.25	5.63	1.31	43.81	0.67	1.37	43.94
180	4	47.67	5.98	0.00	46.36	0.73	1.50	-

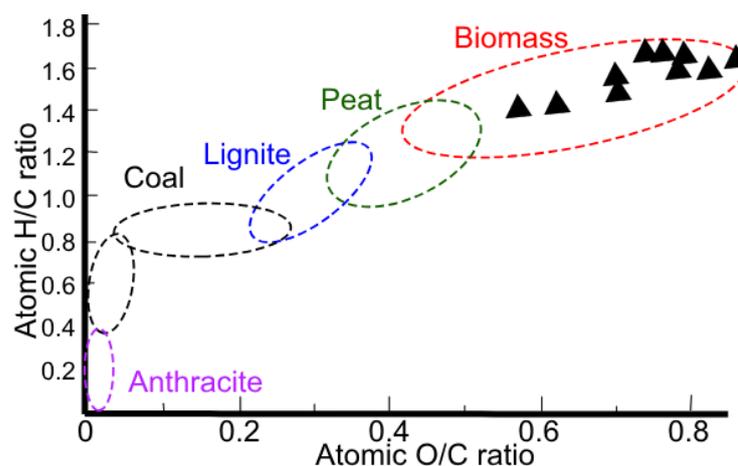


Figure 9. Characterization of the solid phase via the van Krevelen diagram.

On the other hand, after the hydrothermal valorization processes, the C/N ratio varies towards a decrease in the decomposition rate via the use of microorganisms, making the biochar obtained not optimal for the processes of the microorganism diet for transformation or fermentation.

3.3. Valorization via Hydrothermal Carbonization (HTC)

Figure 10 shows the preliminary follow-up of the potential presence of acids or charged species, as explained previously for LHW. The pH shows a minimum at 200 °C, suggesting that the maximum yield of a specific acid is obtained under those conditions; this was later confirmed by the HPLC-RI quantification, where at 200 °C a maximum of levulinic acid and a high concentration of formic acid are observed. Similarly, Figure 10b shows that the conductivity of the system has a maximum of 200 °C, and after that, it starts to decrease. This can be attributed to the lower yield of levulinic acid concentrations at higher concentrations due to the degradation of smaller molecules.

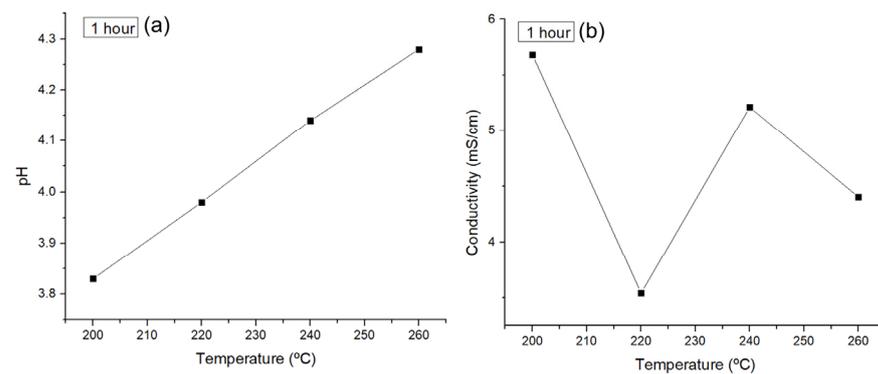


Figure 10. Preliminary follow-up of the content of platform chemicals via HTC. (a) pH vs temperatures (b) Conductivity vs temperature.

3.3.1. Quantification of Liquid Fractions

The preliminary follow-up is confirmed by the quantification and yields obtained via HPLC-RI (Table 10). The highest total yield is obtained at 260 °C due to a high concentration of formic acid and the presence of sugars and levulinic acid, as well as a higher amount of liquid fraction remaining after the hydrothermal processes, which makes for more grams of platform chemicals (PC) obtained from the same amount of initial biomass.

Table 10. Quantification and yields of platform chemicals obtained via HTC.

T (°C)	Concentration PC (g/L)					Yield (%w)
	Sugars	Levulinic Acid	Formic Acid	HMF	Furfural	
200	0.720	1.908	7.868	0.523	0.447	44.182
220	0.520	1.621	8.299	0.046		47.541
240	0.514	1.111	9.291			48.664
260	0.428	0.885	9.739			49.469

At temperatures between 200 and 220 °C, HMF and furfural are obtained, but the total yield is lower due to hydration reactions that take place to form the previously mentioned PC. This makes for a lower amount of liquid fraction at the end of the hydrothermal reaction and, hence, lower yields. The production of HMF, furfural, sugars, and levulinic acid starts to decline at 220 °C (Figure 11) because sugar is being transformed into the other PC, but these compounds continue to react due to the high energy system and cannot stop in the desired products and continue to hydrate and degrade into smaller molecules such as formic acid.

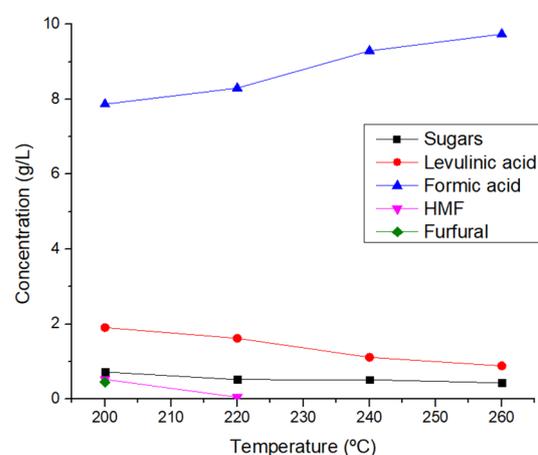


Figure 11. The concentration of platform chemicals obtained via HTC.

3.3.2. Characterization of Solid Fractions Infrared Spectroscopy of HTC Solid Fractions

Figure 12, the IR spectra of HTC solid fractions, shows a bigger change compared to the previously presented Figures 8 and 9. In this case, the band of O-H vibrations of H-bonded hydroxyl groups at around 3332 disappears due to the elimination of said functional groups from the liquid fraction. Similarly, the signals in 1027 cm^{-1} (symmetrical C-O-C, C-OH, and C-O vibrations of cellulose, hemicellulose, and lignin), 1516 cm^{-1} (C=C vibrations, indicative of lignin and aromatic C), 1625 cm^{-1} (C=C vibrations of aromatic compounds), and 1730 cm^{-1} (C=O vibrations of ketone, aldehyde, and acid groups) disappear with higher temperatures. This is due to the hydrolysis of the lignocellulosic structures and the formation of PC and the initial acquisition of biochar-like solids.

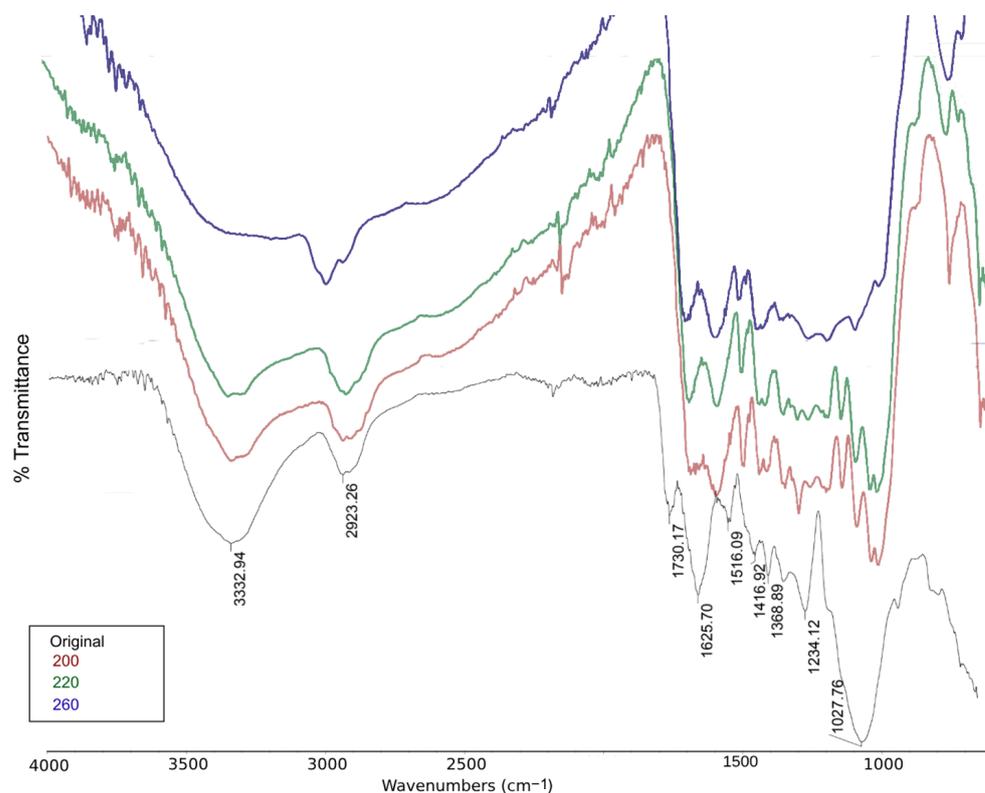


Figure 12. Infrared spectra of solid fractions obtained via HTC valorization.

Elemental Analysis of HTC Solid Fractions

The elemental analysis of the solid fractions is reported in Table 11. By applying the valorization via HTC, an important increase in the percentage of carbon takes place, as well as a loss of oxygen from the initial biomass, which is extracted into the liquid fraction. These changes affect the O/C and H/C ratios for the characterization of the biomass.

Table 11. Elemental analysis of solid fractions obtained via HTC.

T (°C)	%C	%H	%N	%O	O/C	H/C	C:N
	43.33	5.95	1.71	49.02	0.85	1.65	29.65
200	60.88	5.72	1.42	31.98	0.39	1.13	50.02
220	72.10	4.32	1.09	22.49	0.23	0.72	77.17
240	76.12	4.11	1.10	18.67	0.18	0.65	80.73
260	78.81	3.43	0.88	16.88	0.16	0.52	104.48

In Figure 13, the final characterization of each solid fraction is shown, where, in contrast to the LHW process, the initial biomass undergoes important changes assimilating

the structure of coals, lignites, and peat. Coal, a form of carbonized biomass, is primarily used for energy production, contributing to over a quarter of global energy production. Lignites, which are intermediate stages in the formation of coal, can be used as a feedstock for the chemical industry and as a source of fuel. Peat is used in various applications, such as fuel, chemical production, and environmental remediation. In the context of biomass valorization, coal, lignite, and peat can serve as potential sources of carbon and energy, providing a basis for the development of new materials and chemicals derived from these biomass types. This shows that not only a valuation is taking place through the production of platform chemicals but also for the acquisition of solid fuels of interest in the industry.

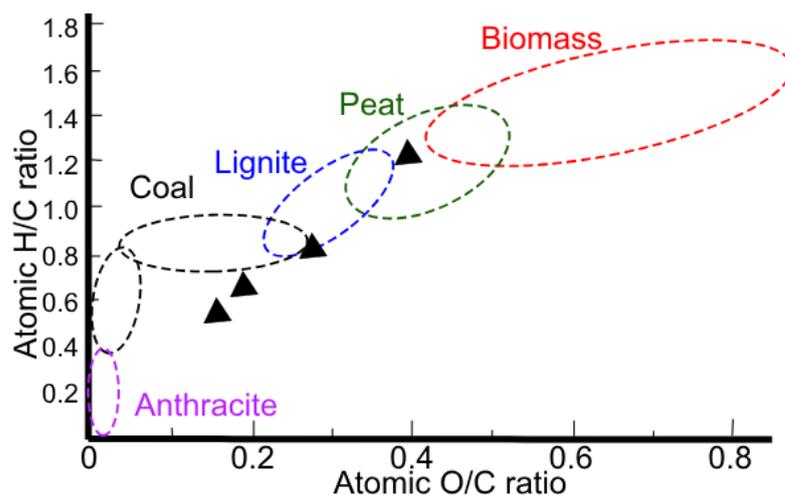


Figure 13. Characterization of the solid phase obtained by HTC via a van Krevelen diagram.

3.4. Optimization and Catalysts

3.4.1. Catalysts

The use of catalysts in the hydrothermal valorization of biomass is of significant importance. Catalysts play a crucial role in enhancing the efficiency of biomass conversion processes, such as hydrothermal liquefaction, by promoting the decomposition of complex organic molecules into simpler, more valuable compounds. They can improve the selectivity of product formation, increase reaction rates, and lower the operating temperatures and pressures required for the conversion process. Table 12 shows the comparisons of the outcomes of PC with and without catalysts. The use of H_2SO_4 as a catalyst breaks the glycosidic bonds in hemicellulose under relatively mild treatment conditions, resulting in the release of sugars and other hemicellulose components. The acid hydrolysis of lignocellulosic biomass with sulfuric acid is an efficient method for the generation of monomeric sugars, which can be further processed into biofuels, chemicals, and other value-added products. The highest concentration of sugars is obtained using sulfuric acid as a catalyst in one hour, but it also produces HMF after 1 h of reaction, an aspect that is only achieved with this catalyst. After two hours of reaction, sulfuric acid leads to the formation of HMF and a decrease in sugars and levulinic acid.

The use of a weak acid catalyst (CH_3COOH) changes the reaction process, leading mostly to the production of formic acid in the first hour of the reaction. After two hours of reaction time, the energy induced by the system degrades formic acid but allows the existing sugars to transform into levulinic acid, producing a great increase in the production of levulinic acid compared to that obtained without a catalyst.

The use of both weak and strong basic catalysts in the first hour does not help with the hydrolysis process, producing a low concentration of sugars and an important concentration of formic acid with NaHCO_3 . After increasing the time, KOH allows the formation of furfural in 2 h, which is not achieved without catalysts but significantly decreases the

production of sugars. On the other hand, NaHCO_3 continues to increase sugar production but also yields an important amount of formic acid selectively.

Table 12. Concentration and yields of platform chemicals obtained with catalysts.

Time	Catalyst	Concentration PC (g/L)					Yield (%w)
		Sugars	Levulinic Acid	Formic Acid	HMF	Furfural	
1	NO	34.818	0.577				70.001
1	H_2SO_4	36.363	0.785		0.619		59.668
1	CH_3COOH	20.660		18.394			73.003
1	KOH	16.498					21.938
1	NaHCO_3	13.876		9.976			43.144
2	NO	26.341	1.063	2.392	0.299		62.284
2	H_2SO_4	23.182	0.769		1.059		39.755
2	CH_3COOH	14.518	5.152		1.097		53.488
2	KOH	1.791	1.896	9.351	0.761	1.146	50.178
2	NaHCO_3	20.753		23.953			81.427

3.4.2. Optimization

Figure 14 shows the optimal conditions for the production of sugars from pea pod waste. It shows that even though the concentration of sugars obtained is the highest using H_2SO_4 as a catalyst, the amount of liquid phase obtained at 180 °C for 1 h without catalyst is greater, making the yield bigger as well. At higher temperatures and longer reaction times, the sugars react to produce the other PC or undergo degradation, which makes the yield decrease. The best conditions would then be at 180 °C for one hour with H_2SO_4 as a catalyst or without it. If the process is meant to be cleaner, then it is suggested to not implement the catalyst, as a good yield is obtained without its use.

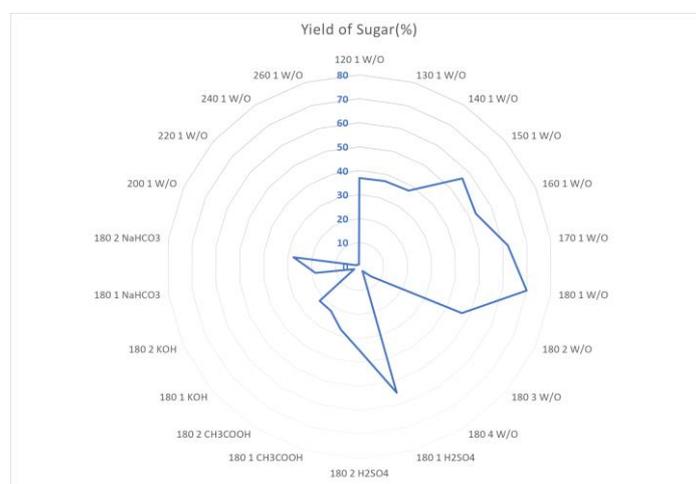


Figure 14. Optimization of conditions (temperature (°C), time (h), and catalysts) for the obtention of sugars. W/O = Without.

The yield of formic acid production (Figure 15) is highly influenced by high temperatures and the use of catalysts, obtaining the best results under the conditions of 180 °C, 2 h, and NaHCO_3 as a catalyst. Good yields are also achieved using CH_3COOH as a catalyst at 180 °C or at 260 °C without a catalyst. It is suggested then, in order to achieve a good yield of formic acid, to use weak acids or bases as catalysts for the process for longer times, or, in the case of the use of only water, higher conditions of HTC favor the degradation of other PC to formic acid.

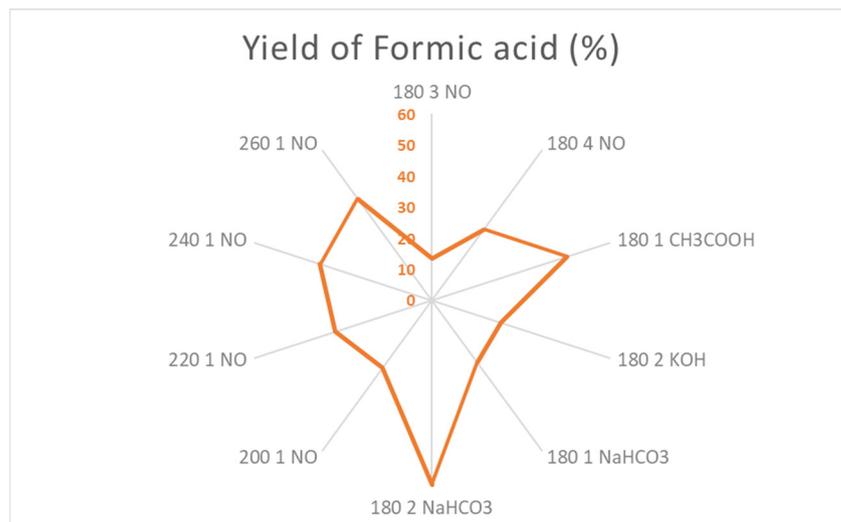


Figure 15. Optimization of conditions (temperature (°C), time (h), and catalysts) for the obtention of formic acid.

Levulinic acid's optimal conditions for production are reported in Figure 16. The use of weak acid catalysts and longer reaction times (2 h) favor the formation of levulinic acid remarkably. Temperatures over 200 °C but under 260 °C also produce high yields of levulinic acid without the need for catalysts, with 200 °C being the best condition. At temperatures above 260 °C, the acid starts to degrade into smaller molecules, decreasing the yield.

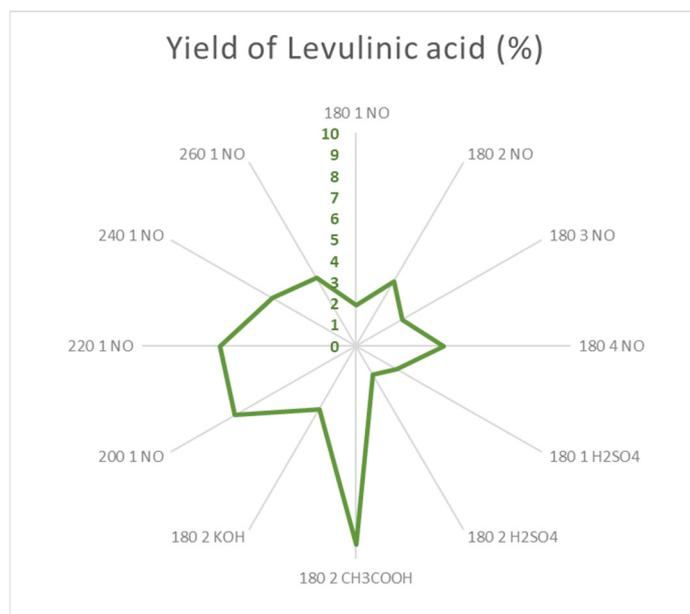


Figure 16. Optimization of conditions (temperature (°C), time (h), and catalysts) for the obtention of levulinic acid.

Finally, Figure 17 shows the optimal conditions for HMF and furfural production. On this platform, chemicals can be highly unstable, and precise conditions are needed for them to be produced. The use of catalysts helps produce HMF and furfural in shorter times, but the yield is not the best possible. On the other hand, the use of higher reaction times at 180 °C allows for the obtention of higher yields due to the softer conditions for the reactions to take place. At higher temperatures (220–260 °C), the conditions are too strong for this PC to be stable, and they degrade into other products that are not of interest.

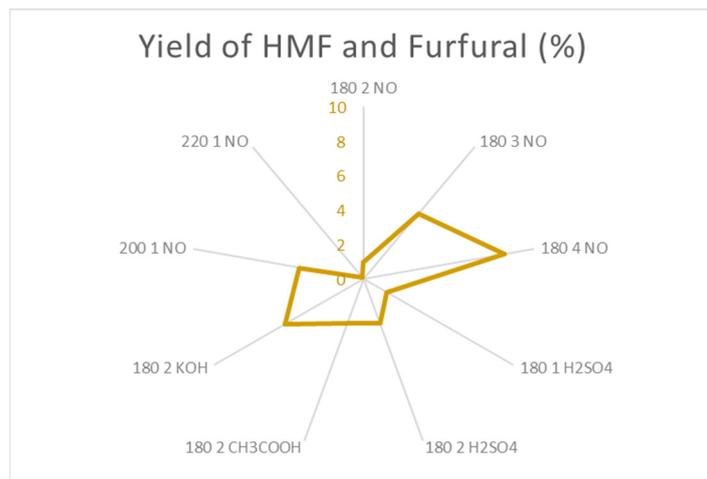


Figure 17. Optimization of conditions (temperature ($^{\circ}\text{C}$), time (h), catalysts) for obtention of HMF and furfural.

4. Conclusions

It was concluded that the pea pod has a high content of volatile matter, which can be transformed into PC due to the presence of organic groups as well as an important amount of fixed carbon, which influences the production of biochar. As for the ultimate analysis, it allowed the characterization of pea pod wastes as biomass according to the van Krevelen diagram, and its C/N ratio showed potential valorization via microorganism implementation. Moreover, the structural analysis presented 20% cellulose, 17% hemicellulose, and 5% lignin. The high content of cellulose and hemicellulose, added to the low amount of lignin, are the best conditions due to the high presence of starting materials that could be transformed into PC and the low possibility of inhibition due to the lignin content.

Valorization via LHW leads to the formation of sugars and levulinic acid at temperatures of 170–180 $^{\circ}\text{C}$, and the highest yield was obtained at 180 $^{\circ}\text{C}$ for 1 h. Reactions at 180 $^{\circ}\text{C}$ for longer times caused the decrease in sugars due to their transformation into other platform chemicals and the formation of formic acid, HMF, and furfural, being the condition with the most variety of platform chemicals. The solid fraction produced in this range of hydrothermal valorization was characterized as biomass and did not change greatly compared to the initial biomass.

The HTC range of hydrothermal valorization caused a significant decrease in the production of sugars because of their complete transformation or degradation into other chemicals. Higher temperatures caused a decrease in levulinic acid, HMF, and furfural, as well as an increase in formic acid caused by the instability of the previously mentioned compounds and their degradation into smaller PCs such as formic acid. The solid fraction produced was characterized as peat, lignite, and coal, which can be used as source energies as well and show a marked difference when compared to the initial biomass.

The use of catalysts helps improve the yields of specific PCs such as formic acid and levulinic acid to make the hydrothermal reactions more specific, but in the case of sugars, HMF, and furfural, the use of catalysts is not necessary, and higher yields can be obtained by longer-term reactions without catalysts. The optimal conditions for each platform chemical were also reported and described in order to provide a guide for the implementation of pea pods as a source of new chemical products, showing that each platform chemical requires specific conditions that favor their production selectively.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app14062329/s1>, Figure S1: LHW batch 100 mL reactor for hydrothermal processes. Figure S2: HTC 500 mL reactors for hydrothermal valorization. Figure S3: Overview of the kinetics of hydrolysis by mathematical treatments.

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