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Optimization of the Waste Lignocellulosic Biomass Hydrothermal Carbonization Process by Response Surface Methodology

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In recent years, various thermochemical processes have been studied to obtain bioenergy. Hydrothermal carbonization (HTC) has proven to be a convenient alternative since it allows biomass with high moisture and ash content to be processed without prior drying processes, obtaining a biofuel with up to 20 to 30 % more calorific value compared to biomass. However, the main challenge is determining optimum points of increase in calorific power and energy performance to transform it into economically feasible. This study proposes the study and optimization of the HTC process with two Chilean biomasses: sawdust (*Pinus radiata*) and rapeseed (*Brassica napus*). Mass yield (MY), higher heating value (HHV), and energy yield (EY) were analyzed by applying a Design of Experiments (DoE) with three factors and two levels (2^3). The variables used and their levels were temperature (T): 190 - 250 °C; time (t): 60-120 min; and biomass/water ratio (B/W): 8 – 14 % for rapeseed and 10 – 16 % for sawdust. For sawdust, increasing the temperature from 190 to 250 °C raised HHV by 23 % and lowered MY (by 21 %) and EY (by 18 %). Rapeseed HHV showed an increase of 23 %, while MY and EY decreased by 11 and 14 %. In the statistical analysis, the most influential variables for both biomasses were temperature and the B/W ratio, similar to what was found in previous studies. New operating points were determined to maximize the HHV of the hydrochar using the Response Surface Methodology and the equations obtained from the DoE (R^2 above 0.98). The results achieved were higher than the average indicated in the literature. For sawdust, an EY of 77 % and an HHV of 28.6 MJ/kg (+48 %) were obtained at 280 °C, 100 min, and a B/W of 13 %. On the other hand, for rapeseed, EY=49.2 % and HHV=29.1 MJ/kg (+37 %) were achieved at 280 °C, 90 min, and a B/W ratio of 10 %.

1. Introduction

Global energy demand has caused a sustained increase in fossil fuel consumption. Data from the World Bank updated to 2018 indicate that more than 3,100 kWh per capita of energy are consumed annually worldwide. As a result, about 34 Gt of CO_2 and other greenhouse gases contribute to climate change yearly (IEA, 2021). In the case of Chile, the non-renewable energy contribution has been between 68 and 78 % in the last decade, and with high levels of pollution by PM_{10}, $PM_{2.5}$, and sulfur oxides (Puentes et al., 2021). In addition, about 75 % of the productive matrix comes from non-renewable sources (Ministerio de Energía, 2015). The use of firewood and biomass represents 25 % of the total energy in the country, although it only contributes 4 % of the total electricity. This difference is because biomass is mainly used for heating and cooking (Murillo et al., 2022).

On the other hand, a sustained increase in energy production from renewable sources can be observed. In the case of electricity, without hydroelectric production, Chile has increased the kWh generated by four times

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between 2010 and 2015 (IEA, 2021). The policy approved at the national level establishes that by the year 2050, at least 70 % of electricity generation must come from renewable energies (Ministerio de Energía, 2016).

With this background and considering the current global energy situation, the search for new energy sources is being carried out with greater depth and speed. According to 2010 forecasts, oil reserves are sufficient for about 50 years for global power generation. However, due to the high environmental pollution caused, it is not feasible to continue consuming oil at the current rate, which generates the possibility that clean and renewable energies will enter the scene as leading actors in the short term (Xu et al., 2020). Finally, another critical aspect is that Chile is the largest producer of garbage in Latin America, per person and per day, with low recycling rates and an extractivist economic model, like other countries in the region (González-Arias et al., 2021). It is a scenario with extensive challenges and opportunities to implement circular economy processes since biomass is an energy source with great potential, with more than 220 Gt of dry biomass (4,500 EJ) generated annually, equivalent to 8 times the global energy requirement (Baloch et al., 2018).

Compared to fossil fuels, biomass is a carbon-neutral raw material capable of generating sustainable processes at an industrial level (Ryu et al., 2020). Moreover, biomass is abundant and widely available worldwide, with fast replacement and regeneration periods, low sulfur content, and ease of transport, making it one of the raw materials with the best projection within the possible sources of energy in the short and long term (Patel and Kumar, 2016). As a result, bioenergy corresponds to 16 % of the total renewable energy produced annually (2016) and is expected to reach 50 % by 2050 (Jain et al., 2022).

The use of wood pellets entails a series of benefits over the use of firewood, such as its higher density, lower transport and storage costs, and its higher energy density with a minimum of 18 MJ/kg and fewer emissions due to its lower humidity (<10 %) (Erses Yay et al., 2021). However, the fast humidification of the pellets is due to the high relative humidity of urban areas where it is mainly used, generating incomplete combustion and affecting air quality. It has been reported that wet pellets produce 140 times more fine particulate matter ($PM_{2.5}$) than natural gas (Guerrero et al., 2019). An alternative that has shown promising results with different types of biomass is hydrothermal carbonization (HTC). HTC has the advantages of a lower operating temperature compared to traditional torrefaction and other biomass conversion technologies and its ability to work with biomass with high moisture content (> 20 %) (Blach and Engelhart, 2021). This process converts biomass into biofuel with a higher calorific value, hydrophobic properties (Vallejo et al., 2021), and less ash content (McGaughy and Reza, 2018).

2. Materials and methods

2.1 Characterization of biomass and hydrochar

In this study, the biomasses used were the residues of the canola rapeseed pressing process (RPS) and radiata pine sawdust (AS). Both biomasses were obtained in the south of Chile in the cities of Temuco and Gorbea and used as received. The moisture content (M) of each biomass and the hydrochar obtained was determined following the ISO 18134-2 standard (ISO, 2017). The determination of the calorific value (HHV) was carried out with a Parr 6200 calorimeter. The ash content (A) was calculated following the ISO 18122 standard (ISO, 2016). In addition, it was determined the mass content of carbon (C), hydrogen (H), nitrogen (N), and oxygen (O). For the proximate analysis, the values of lignin (L), cellulose (C), hemicellulose (H), and aqueous extracts (AE) have been reported in previous studies (Vallejo et al., 2019). Table 1 shows the characterization of each biomass.

2.2 Hydrothermal carbonization

The hydrothermal treatment was carried out using a high-pressure 5 L stainless steel reactor (model HiPR-SF5L). Raw biomass and water were loaded, and before closing the reactor, gaseous nitrogen was injected to ensure an inert atmosphere. Once the reactor was closed, the temperature was gradually increased until the reaction temperature was reached. This temperature must remain constant during the HTC reaction time. Then, the reactor was cooled down at around 30 °C, and the gas phase was purged before the reactor was opened. The hydrochar was collected from the reactor and then filtrated to separate it from the liquid phase. All collected samples were dried using a forced air oven at 105 °C for 24 h for subsequent analysis.

Table 1: Raw biomasses characterization

Biomass	M (%)	Proximate analysis					HHV	Ultimate analysis			
		A (%)	L (%)	C (%)	H (%)	AE (%)	(MJ/kg)	C (%)	H (%)	N (%)	O (%)
AS	57.87	0.21	30.0	42.0	25.0	2.79	19.28	48.8	6.2	0.13	44.8
RPS	7.14	6.25	36.3	10.3	35.3	11.9	21.36	49.7	6.9	5.30	30.8

2.3 Experimental design and optimization

A full factorial 2^3 design was applied for each feedstock which considered three factors that widely influence the HTC process according to literature: temperature, time, and biomass/water ratio (B/W) (Vallejo et al., 2020b). Mass yield (MY), higher heating value (HHV), and energy yield (EY) were the response variables assessed in this work. The used levels for each factor are shown in Table 2. Eq(1) shows the mass yield calculation. The energy densification ratio is determined in Eq(2), and the energy yield is defined by Eq(3).

Table 2: Factors and levels in experimental design

B/W (%w/w)		Time (min)	Temperature (°C)	AS - ID	RPS - ID
AS	RPS				
10	8	60	190	PR - 1	R - 1
			250	PR - 2	R - 2
		120	190	PR - 3	R - 3
			250	PR - 4	R - 4
16	14	60	190	PR - 5	R - 5
			250	PR - 6	R - 6
		120	190	PR - 7	R - 7
			250	PR - 8	R - 8

The effect of the process variables was examined by the response surface methodology (RSM) that allowed to attain models for describing the behaviour of the response variables. The selected time and temperature values were based on previous works. The temperature range was selected based on the expected decomposition of each macromolecular fraction, according to Vallejo et al. (2020a), at 190 °C, the degradation of hemicellulose begins, and at 250 °C the conversion of cellulose into short chains is observed. The B/W ratio was different in both biomasses due to the initial humidity of the biomass: sawdust (57.9 %) and rapeseed (7.1 %) and the reactor volume.

$$MY = \frac{m_H}{m_B} \cdot 100 \tag{1}$$

$$EDR = \frac{HHV_H}{HHV_B} \tag{2}$$

$$EY = MY \cdot EDR \tag{3}$$

where m_H and m_B are the mass of the dry hydrochar and the dry raw biomass, HHV_H and HHV_B are the higher heating values of the hydrochar and the raw biomass.

3. Results and discussion

3.1 Design experimental

The results achieved for rapeseed are shown in Figure 2. The mass yield values are between 40 and 55 % because the aqueous extractives decompose before reaching 180 °C, and the hemicellulose has many reaction pathways between 180 and 230 °C, as reported in a previous study (Vallejo et al., 2020). The rapeseed present 47.2 % of hemicellulose (H) and aqueous extractives (AQ). On the other hand, the sawdust has 27.8 % between both fractions, which explains why the mass yields were between 55 and 83 %, as shown in Figure 3. The selection of the levels and factors studied in the experimental design was adequate since increases in calorific values of 37, and 39 % were obtained at 250 °C and 120 min for rapeseed and sawdust. This increase has been achieved only with a few biomasses previously treated with HTC and reported in the literature. For example, the Tahoe mix increased by 45 % and loblolly pine by 43 % when subjected to 290 °C and 30 min (Hoekman et al., 2017). Maize silage showed a 60 % increase in HHV at 200 °C and 6 h (Reza et al., 2014), and beech wood reported a 94 % increase in HHV at 220 °C and 17 h (Stemann and Ziegler, 2011).

Reported experiments during the last five years have demonstrated the tendency to decrease the mass yield and increase the calorific value of carbonized biomass when the raw material is treated at higher times and temperatures (Sabio et al., 2016). However, the relationship between both and their synergistic effect has not been fully elucidated since a considerable decrease in mass yield also causes a lower energy yield. So, finding the optimal point for each biomass is crucial to ensure the process's future scalability. Various authors (Lucian and Fiori, 2017) have shown that temperature is the main factor to be analyzed since its influence is simultaneously the most significant in mass yield and calorific value. Indeed, the MY and EDR of rapeseed and sawdust are strongly affected by temperature, as confirmed by regression equations indicated in Table 3.

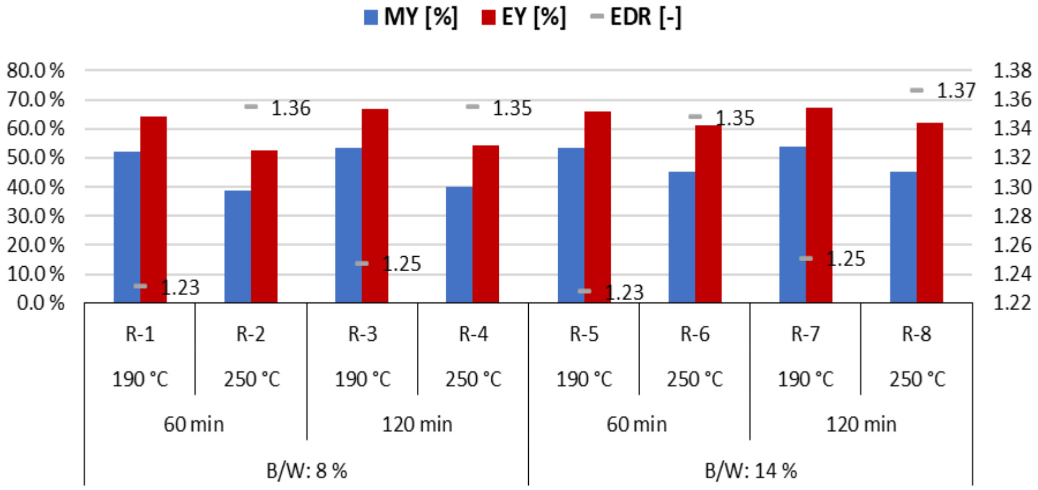

Figure 2: Energy densification ratio, mass, and energy yield for rapeseed

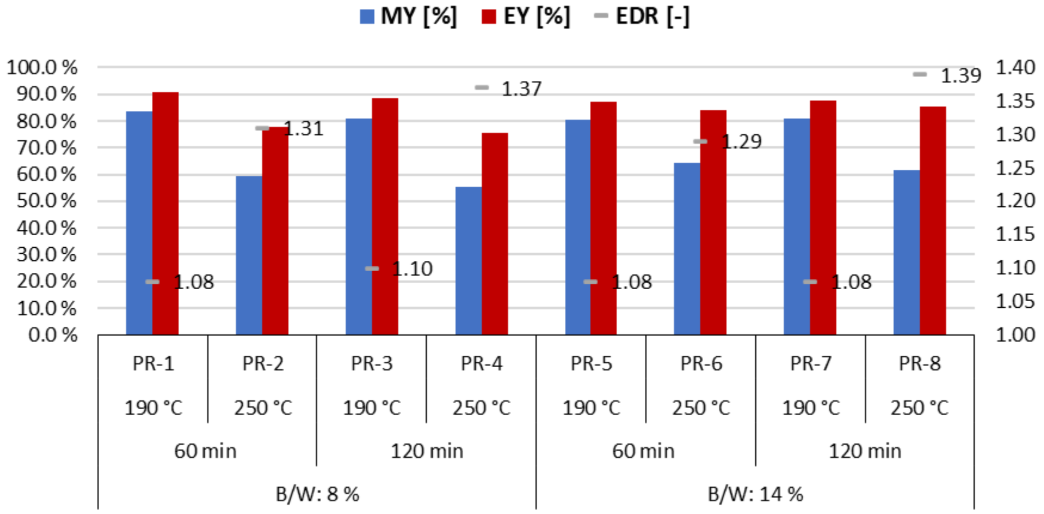

Figure 3: Energy densification ratio, mass, and energy yield for pine sawdust

Table 3 indicates that temperature has the most significant impact in all cases, followed by the biomass: water ratio. Time and its interaction with temperature were significant in the case of the calorific value of sawdust. In general, the R^2 was more significant than 0.99, indicating that the variables analyzed made it possible to explain the experimental results obtained and reliably analyze the sample space resulting from their interactions.

3.2 Operational conditions optimization

The main challenge of the HTC process, like other bioconversion technologies, is its scalability, which is influenced by the quality of the biofuel obtained: HHV, ash content, and physical characteristics. In this work, the optimization of the HTC was carried out by maximizing the EDR. It should be noted that the residence time can be any value within the range studied. The average time of 90 -100 was selected for both biomasses. The rapeseed at 250 °C, 90 min, and 9 % B/W presented a 37 % increase in HHV with an EY of 54.25 %. For sawdust, the result obtained at 280 °C, 100 min, and B/W of 13 % was 48 %, with an EY of 76.75 %, as shown in Table 4.

Sawdust reaches a 48% increase in calorific power at 280 °C and 100 min, something only comparable to that achieved by other biomasses in more extended periods and with higher temperatures, as explained in the previous section. In the case of rapeseed, the optimal point is within the experimental domain already studied. Despite obtaining a higher HHV than sawdust, the mass yield (MY) was more influential due to its macromolecular composition. Indeed, the cellulose content of sawdust (42 %) indicates a higher thermal resistance to temperature change than raps (10 %). Finally, both biomasses have more than 30 % lignin, which explains their high calorific value (Vallejo et al., 2020a).

Table 3: Experimental design and coefficients obtained for the significant effects

Biomass	RV	Response relation	R^2
AS	MY	$70{,}86 - 10{,}53 \cdot x_T + 1{,}13 \cdot x_R + 1{,}91 \cdot x_T \cdot x_R$	0.9808
	HHV	$23{,}37 + 2{,}42 \cdot x_T + 0{,}43 \cdot x_t + 0{,}35 \cdot x_T \cdot x_t$	0.9957
	EY	$84{,}51 - 7{,}76 \cdot x_T + 2{,}91 \cdot x_R + 5{,}18 \cdot x_T \cdot x_R + 1{,}57 \cdot x_t \cdot x_R$	0.9963
RPS	MY	$47{,}81 - 5{,}45 \cdot x_T + 1{,}68 \cdot x_R + 1{,}26 \cdot x_R \cdot x_T$	0.9931
	HHV	$27{,}7267 + 1{,}2456 \cdot x_T$	0.9795
	EY	$61{,}84 - 4{,}39 \cdot x_T + 2{,}17 \cdot x_R + 0{,}79 \cdot x_t + 1{,}86 \cdot x_R \cdot x_T$	0.9975

Table 4: Optimal operational conditions for pinus radiata and rapeseed

Biomass	Temperature (°C)	Time (min)	B/W (%)	HHV (MJ/kg)	MY (%)	EDR (-)	EY (%)	Error (%)
AS	280	100	13	28.53	50	1.48	76.75	2.5
RPS	250	90	9	28.97	40	1.37	54.25	3.2

4. Conclusions

Experimental results using a complete factorial experimental design elucidated that in the HTC process of sawdust and rapeseed at a laboratory scale, the statistically significant factors on the response variables MY, HHV, and EDR were the biomass/water ratio and temperature. The most significant impact in all the response equations was the temperature. The time was insignificant for the response variables, indicating that 60 min optimal results can be achieved, reducing the residence time. In addition, it was established that for sawdust, the operating conditions that maximize EDR (+48 %) were at 280 °C, 100 min, and B/W of 13 %. While for rapeseed, it was defined that the operating point that maximizes the EDR (+37 %) was at a temperature of 250 °C, 90 min of reaction, and a biomass/water ratio of 9 %. The relevance of the temperature and B/W ratio interaction will allow the scalability of the process in the future, and a more profound study about the energy consumption for heating the water to subcritical conditions must be carried out. Finally, the optimal operating conditions achieved in this study have improved the efficiency of the process concerning biomass and similar experimental conditions previously reported, indicating sawdust is a promising raw material for performing a process with high efficiency at pilot and industrial levels.

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