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The effect of magnesium chloride as an additive of hydrothermal carbonization (HTC) of lignocellulosic biomass (*Pinus radiata* sawdust) was studied. The HTC tests were carried out at fixed conditions of temperature and residence time of 220 °C and 1 h, respectively, and varying the dose of magnesium chloride in the range 0.0?1.0 g MgCl₂/g biomass. The carbonized product (hydrochar) was tested in order to determine its calorific value (HHV) while using PARR 6100 calorimeter, mass yield by gravimetry, elemental analysis using a LECO TruSpec elemental analyzer, volatile matter content, and ash content were obtained by standardized procedures using suitable ovens for it. The results show that using a dose of 0.75 g MgCl₂/g biomass results in an impact on the mass yield that was almost equal to change operating conditions from 220 to 270 °C and from 0.5 to 1 h, without additive. Likewise, the calorific value increases by 33% for this additive dose, resulting in an energy yield of 68%, thus generating a solid fuel of prominent characteristics.

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Article

Experimental Study on Hydrothermal Carbonization of Lignocellulosic Biomass with Magnesium Chloride for Solid Fuel Production

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Abstract: The effect of magnesium chloride as an additive of hydrothermal carbonization (HTC) of lignocellulosic biomass (*Pinus radiata* sawdust) was studied. The HTC tests were carried out at fixed conditions of temperature and residence time of 220 °C and 1 h, respectively, and varying the dose of magnesium chloride in the range 0.0–1.0 g MgCl₂/g biomass. The carbonized product (hydrochar) was tested in order to determine its calorific value (HHV) while using PARR 6100 calorimeter, mass yield by gravimetry, elemental analysis using a LECO TruSpec elemental analyzer, volatile matter content, and ash content were obtained by standardized procedures using suitable ovens for it. The results show that using a dose of 0.75 g MgCl₂/g biomass results in an impact on the mass yield that was almost equal to change operating conditions from 220 to 270 °C and from 0.5 to 1 h, without additive. Likewise, the calorific value increases by 33% for this additive dose, resulting in an energy yield of 68%, thus generating a solid fuel of prominent characteristics.

Keywords: hydrothermal carbonization; waste to energy; additives; lignocellulosic biomass; magnesium chloride

1. Introduction

In developing countries, the economy is mainly based on the extraction of raw materials, so, in recent years, the importance of diversifying the energy matrix has been discussed. The considered alternatives include the use of energy obtained from biomass (bioenergy), due to its lower impact on climate change and air pollution and, therefore, on people's health [1].

Residual biomass is a natural and renewable source of carbon with the potential to replace fossil fuels. The main disadvantages of the use of biomass as an energy source, as compared to fossil fuels, are the higher moisture, volatile, and oxygen content. Additionally, biomass has less elemental carbon content and, therefore, a lower calorific value [2], which generates an increase in air pollution by particle emission due to inefficient combustion of residential biomass in several cities around the world [1,3–5].

Research of new technologies to obtain bioenergy aims to improve the energy characteristics of the final product, obtaining a more attractive and cleaner fuel. Some reported techniques include drying biomass before use in power generation systems [6], pellet densification [7], acid washing and subsequent pyrolysis [8], co-combustion with coal [9], and torrefaction [10]. All of these processes have had relatively positive results.

In the last decade, a process that substantially improves the energy content of biomass, known as hydrothermal carbonization (HTC) or wet torrefaction, has been studied. HTC is a thermochemical biomass conversion process that generates a solid product, which is called hydrochar. This product has hydrophobic properties and a greater higher heating value (HHV) when compared to the untreated biomass. The process is carried out in a batch or continuous reactor with the biomass in the presence of liquid water as the reaction medium and in an inert atmosphere. The reaction temperature might vary in the range of 180 to 300 °C and under autogenous pressure conditions [11].

HTC can treat any biomass without the need to dry it previously, being one of the main advantages of the process. However, the mechanisms of the different conversion reactions that the biomass constituents get through must be explained in the future. The molar elemental fractions of H/C and O/C in the Van Krevelen diagram can show what biomass reactions undergo in the HTC process. The direction of the route registered by the points before and after the operation can predict the reactions of demethylation, decarboxylation, and dehydration. Other conversions that occur are the total breakdown of hemicellulose and partial breakdown of cellulose. These reactions generate a loss of solid mass, considerably concentrating the carbon content of the final product and, therefore, an increase in HHV. The by-products of the process are a gas phase, mainly CO₂, and a liquid phase composed of monomeric sugars that are produced by the breakdown of molecules of hemicellulose and cellulose [11].

The HTC process has proven successful in improving the combustible properties of a wide variety of biomass types, such as jeffrey pine and white fir [12], loblolly pine, sugarcane bagasse, corn stover [13], tomato peel [14], olive residues [15], fecal biomass [16], wheat straw [17], grape pomace [18], urban sludge [19], among others. The use of additives and their influence on the performance of mass and energy yields and carbon content is another relatively unexplored area of the HTC process. Lynam et al. [20,21] reported a notable study on this subject, showing exciting results regarding the effect of a variety of organic and inorganic salts in the hydrochar. That study analyzed lithium chloride and acetic acid as additives in the HTC process, obtaining a 30% improvement in hydrochar HHV when compared to biomass without treating the same operating conditions.

This study uses magnesium chloride (MgCl₂) as additive, since lithium and magnesium are closely related due to the isodiagonality that exists in the periodic table, which, by definition, is the similarity in chemical properties between an element and that to the lower right of it in the periodic table [22]. Proof of their behavior is that lithium and magnesium have similar characteristics (such as atomic and ionic radius), form the same types of compounds (nitrites, salts, oxides), and react with the same acids and bases [23].

The main objective of this study is to analyze the effect of magnesium chloride as an additive in the heat treatment of lignocellulosic biomass by HTC, focusing on parameters, such as HHV, mass and energy yields, elemental analysis, and fixed carbon content in the resulting hydrochar.

2. Materials and Methods

2.1. Biomass

The biomass samples (*Pinus radiata* sawdust) were supplied by MAGASA, a Chilean furniture company that is located in Temuco, Chile. This type of residual biomass was chosen due to its abundance in Chile, with estimates of around 5,555,153 m³/year, producing approximately 1,300,748 tons of sawdust per year [24]. Table 1 shows the thermochemical characterization of the biomass. The additive, anhydrous magnesium chloride (USP, purity > 99%, powder) was purchased from a local Chilean supplier (SOVIQUIM, Santiago, Chile).

Table 1. Fuel characteristics of the biomass (*Pinus radiata*).

Parameter	Units	Value *
Proximate Analysis		
Volatiles	%	86.35 ± 0.10
Ash	%	0.21 ± 0.01
Fixed Carbon (balance)	%	13.44
Ultimate Analysis		
Carbon	%	51.55 ± 1.09
Hydrogen	%	5.95 ± 0.05
Nitrogen	%	0.06 ± 0.01
Sulphur	%	0.08 ± 0.00
Chlorine	%	0.012 ± 0.003
Oxygen (balance)	%	42.14
Higher Heating Value (HHV)	MJ/kg	20.11 ± 0.01
Lower Heating Value (LHV)	MJ/kg	18.81

* Results in dry basis, the analyses were performed in triplicate.

2.2. Chemical and Physical Analysis

The biomass and the carbonized final product (hydrochar) were crushed in a 0.5 mm RETSCH centrifugal mill (RETSCH, Haan, Germany), model number ZM200. The volatile content was calculated according to EN-ISO 18123 (2015) while using a Carbolite oven (CARBOLITE GERO, Parsons, UK) model number 12PR/400. The ash content was measured according to EN-ISO 12122 (2016) in a Hobersal oven (FORNS HOBERSAL, Barcelona, Spain) model number AFF1100. The fixed carbon content was obtained as the 100% difference of the two previous measurements. Each analysis was performed in triplicate.

Elemental analyzes of carbon, hydrogen, nitrogen, sulfur, and oxygen (CHONS) were performed on a LECO TruSpec elemental analyzer (LECO, St. Joseph, MI, USA). The samples were burned in a highly oxidizing atmosphere. The combustion gases (CO₂, H₂O, and NO_x) were directed to different cells, in which the individual percentage of each element is calculated. The carbon, hydrogen, and sulfur contents were determined by infrared absorption, while thermal conductivity determined the nitrogen content. The carbon, hydrogen, and nitrogen contents were calculated according to the procedure that is described in EN ISO 16948 (2015), while the sulfur content was calculated according to EN-ISO 16994 (2016). Finally, the oxygen content was obtained as the 100% difference of the carbon contents, hydrogen, nitrogen, sulfur, and ashes previously determined.

The HHV of the materials was evaluated on a Parr calorimeter (Parr Instrument Company, Moline, IL, USA) model 6100, according to the experimental procedure that was described in EN-ISO 18125 (2017).

The mass yield (MY), the energy densification ratio (EDR), and the energy efficiency (EY) were calculated as indicated in the Equations (1)–(3): [25].

$$MY = \frac{\text{dry hydrochar weight}}{\text{dry raw biomass}} \quad (1)$$

$$EDR = \frac{\text{hydrochar HHV}}{\text{raw biomass HHV}} \quad (2)$$

$$EY = MY \times EDR \quad (3)$$

2.3. Hydrothermal Carbonization

The HTC process was carried out in a 3.78 L stainless steel Parr reactor, model number 4551 (Parr Instrument Company, Moline, IL, USA) that was equipped with a stirrer, a pressure gauge, and a proportional-integral-derivative (PID) controller. Figure 1 shows the experimental configuration. The experimental analysis was divided into two parts: (1) study of the influence of time and temperature on the mass yield, to find the best range of operation for the selected biomass. The experiments were carried out in a range of 220 °C (2.32 MPa) and 270 °C (5.5 MPa), and with times of 0.5 and 1 h. With the determination of the best-operating conditions completed, (2) the study of the influence of MgCl₂ as an additive in the range of 0.0 to 1.5 g of MgCl₂/g of biomass. For all HTC tests, the solid to liquid ratio was maintained at 1:12, 100 g of dry biomass, and 1200 g of distilled water. Each experimental run by HTC was identified with the “H_Temperature_Time” tag, with the temperature in Celsius degrees and the time in minutes.

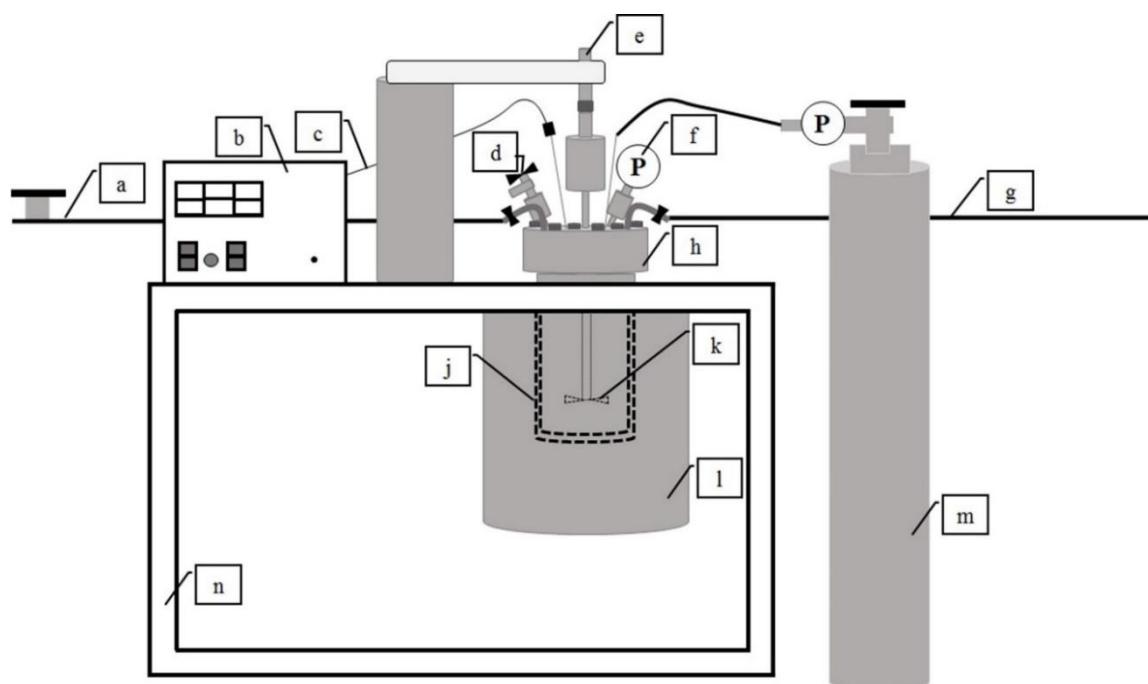


Figure 1. Experimental set-up: (a) Cooling water in, (b) PID controller, (c) Thermocouple, (d) Purge valve, (e) Stirrer Motor, (f) Pressure gauge, (g) Cooling water out, (h) Reactor lid, (j) Reactor vessel, (k) Stirrer, (l) Heating jacket, (m) Nitrogen cylinder, and (n) Reactor support.

The heating time from room temperature to the set-point was approximately 60 min. Once this point was reached, the PID controller maintained the temperature for the necessary time with a variation of ± 2 °C. After the main reaction time, the reactor was cooled through the available cooling coil by feeding it with cold water to rapidly lower the temperature to 30 °C. The gas that was produced

in the reaction was released through the upper reactor valve and the lid was then opened to access the reactor contents. For hydrochar recovery, the reactor contents were filtered using a cloth filter, then dried in an oven at 100 °C for 24 h, and finally stored in airtight bags for later analysis.

3. Results

3.1. Influence of Time and Temperature on Hydrochar Properties

The determination of the best operational point was carried out through several experimental runs to analyze the mass and energy yields and the HHV of resulting hydrochar. Table 2 indicates the detail of the experiences that were carried out to find this best point of operation. The mass yield decreases with increasing reaction time and temperature; this value fluctuates between 45% and 67%.

Table 2. Raw biomass and resulting hydrochar properties.

Experimental Run	Temp °C	Time h	Mass Yield (%)	HHV (MJ/kg)	EDR	EY (%)	Ash (%)
Raw biomass	-	-	-	20.11	-	-	0.21%
H_220_30	220	0.5	66.76%	22.19	1.10	73.67%	0.08%
H_250_30	250	0.5	45.71%	22.87	1.14	51.98%	0.07%
H_270_30	270	0.5	54.90%	23.55	1.17	64.29%	0.07%
H_220_60	220	1.0	66.43%	22.72	1.13	75.05%	0.04%
H_250_60	250	1.0	50.11%	23.17	1.15	57.73%	0.03%
H_270_60	270	1.0	48.86%	23.42	1.16	56.90%	0.04%

All the analyses performed in triplicate and average values are reported; standard deviation $\leq 1.0\%$. Run notation: "H_Temperature (°C)_Time (min)".

The most significant increase in hydrochar HHV is observed at a temperature of 270 °C and 0.5 h of residence time, reaching a value of 23.55 MJ/kg, which is 17% more than the raw biomass. The range of variation of the improvement in HHV is between 10% and 17%. On the other hand, the ash content experimented very similar values in all of the tests carried out, showing a considerable decrease when compared to the untreated biomass.

The biomass is usually composed of hemicellulose, cellulose, lignin, ashes, and aqueous extracts. During the HTC process, the progressive increase in reaction time and temperature causes these components to react through mechanisms that have not yet been fully cleared, since the biomass structure is very complex and the reactions that occur are diverse. On the other hand, aqueous extracts and hemicellulose react from 180 °C, disappearing from the biomass structure at temperatures above 230 °C [26]. Recent studies allow for affirming that, at 150 °C, there are small-scale reactions that hydrolyze some oligomers of the biomass, generating an increase in the carbon content. Above 260 °C, a large proportion of cellulose has degraded, and this results in a rapid drop in mass yield and a greater HHV of the hydrochar [27,28]. These temperature values are relative ranges and they depend on each type of biomass and the HTC process conditions [29]. The best operating point is at 220 °C and 1 h for the pine sawdust treated in this study, since the highest energy yield, 75.05%, is reached, as shown in Table 2. At 250 and 270 °C, EY decreases because MY is below 50%.

3.2. Effect of Magnesium Chloride on Mass Yield

The experimental runs of this section were carried out in two sets maintaining the solid to liquid ratio, at 220 °C and 1 h. The first experimental set was performed with doses of MgCl₂ in large ranges, 0.0, 0.5, 1.0, and 1.5 g MgCl₂/g biomass. In the first experimental set, it was observed that the influence of the additive significantly occurred in the range 0.0–1.0 g MgCl₂/g biomass, so it was decided to continue with a second experimental set to further study this range. This second experimental set was performed with doses of 0.00, 0.10, 0.25, 0.40, 0.50, 0.75, and 1.00 g MgCl₂/g biomass. Figure 2 shows the results.

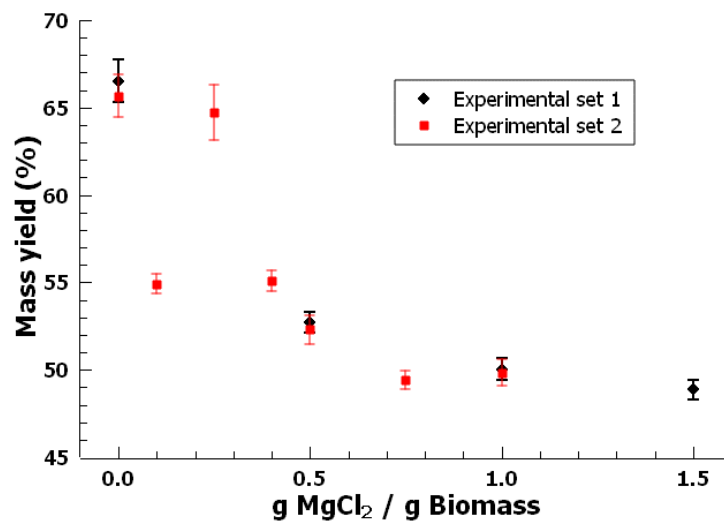


Figure 2. Effect of magnesium chloride on mass yield.

It can be seen that the additive has a significant effect on MY. The lowest value (MY = 50.7%) was obtained for the dose of 0.75 g of MgCl₂/g of biomass. Between this and the execution without additive, there is a difference of 15.7% in this parameter. On the other hand, Table 2 indicates a decrease in the mass yield of 17.9% when the operating process conditions change from 220 °C and 0.5 h to 270 °C and 1 h, without additive. Taking these values into account, the addition of magnesium chloride during the HTC process generates an impact that is similar to that obtained by increasing the temperature by 50 °C and doubling the reaction time.

3.3. Effect of Magnesium Chloride on HHV

Figure 3 shows the effect of the addition of magnesium chloride on HHV. The highest point of HHV is reached at a dose of 0.75 g of MgCl₂/g of biomass, with a value of 26.73 MJ/kg, which implies an improvement of 32.93% in HHV when compared to raw biomass. The increase in HHV did not exceed 16% without the use of additives.

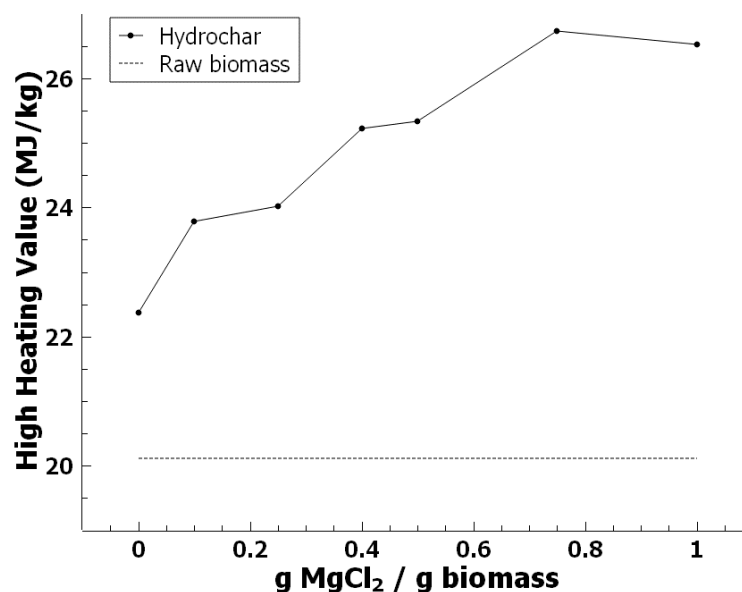


Figure 3. Effect of magnesium chloride on higher heating value (HHV) (all the analyses performed in triplicate and average values are plotted; standard deviation $\leq 1.0\%$).

3.4. Effect of Magnesium Chloride on Energy Yield

Energy yield is one of the most studied variables of the HTC process because of the hydrochar's potential to be used as fuel. Therefore, maximizing the amount of energy of the hydrochar is desirable. However, the increase in time and temperature causes opposite effects on energy efficiency, since its value depends on the mass yield that decreases and the HHV that increases. This optimal point must be determined for each biomass, as noted above.

Lynam, et al. [21] showed that the addition of ionic salts in the same proportion to biomass generated a maximum EY increase of 10%. In this study, a variation of about 9% was obtained between the HTC run without additive and 1 g of MgCl_2/g of biomass, as shown in Figure 4. Besides, it is observed that a dose of 0.25 g of MgCl_2/g of biomass produces an energy efficiency that is 2.6% higher than the condition without additive. Notably, the positive influence on the magnitude of the HHV balances the significant decrease in mass yield, both changes produced by the addition of the additive.

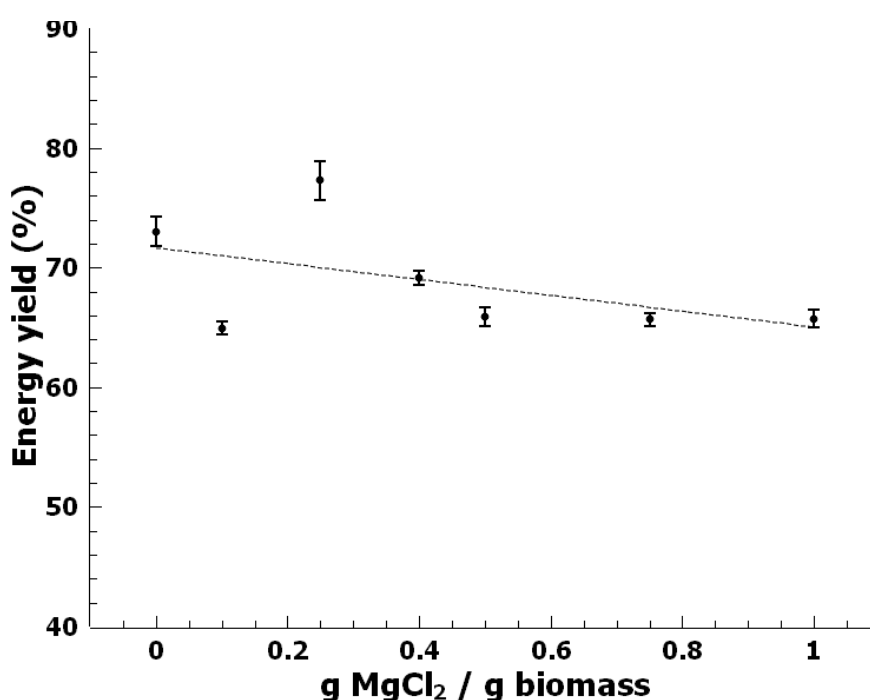


Figure 4. Effect of magnesium chloride on energy yield.

3.5. Effect of Magnesium Chloride on Elemental Fractions

Table 3 shows the final analysis of the carbonized products that were obtained in the experiment. Concerning carbon, the percentage significantly increases in all runs. The dose of 0.75 g of MgCl_2/g of biomass resulted in a hydrochar with the highest percentage of this element, 75.25%, which is 23.34% higher than that of untreated biomass. The hydrogen content also shows significant differences, although they are not entirely correlated with the increase in the dose of the additive. The oxygen content has the highest degree of variation with a dose of 0.75 g of MgCl_2/g of biomass, which leads to a difference of -24.60% as compared to untreated biomass. This difference is beneficial as it increases HHV, as described above. The sulfur content showed significant variations, with the increase in the magnesium chloride dose that led to higher sulfur content. The additive could inhibit the release of sulfur that is present in the biomass, which results in the same amount of sulfur present in the biomass existing in a smaller amount of hydrochar mass, which implies an increase in the sulfur percentage. The nitrogen content did not show significant variations

Table 3. Ultimate analysis of the carbonized product.

MgCl ₂ Dose g MgCl ₂ /g Biomass	%C	%H	%O	%N	%S
0.0	54.83 ± 0.84	6.16 ± 0.03	38.42	0.12 ± 0.01	0.01 ± 0.00
0.1	60.01 ± 0.08	5.28 ± 0.03	33.29	0.13 ± 0.02	0.02 ± 0.00
0.25	62.14 ± 1.21	5.43 ± 0.21	30.32	0.02 ± 0.00	0.02 ± 0.00
0.4	62.69 ± 0.23	5.32 ± 0.00	30.59	0.10 ± 0.01	0.01 ± 0.00
0.5	72.80 ± 0.17	5.82 ± 0.02	16.68	0.05 ± 0.02	0.03 ± 0.00
0.75	75.25 ± 0.22	5.59 ± 0.01	16.21	0.03 ± 0.01	0.03 ± 0.00
1	73.04 ± 0.32	5.67 ± 0.01	19.21	0.20 ± 0.02	0.03 ± 0.00

An excellent way to appreciate the improvement derived from the treatment of hydrothermal carbonization is through an analysis of the Van Krevelen diagram [30], as shown in Figure 5. This diagram shows the typical areas where solid fuels are found, such as lignocellulosic biomass, peat, lignite, coal, and anthracite, depending on the molecular ratio of H/C and O/C that the material under analysis has. It is observed that the hydrochar with a dose of 0.75 g of MgCl₂/g of biomass is in the coal region; therefore, it corresponds to the best result of HTC using the additive. The above is in accordance with the heating value that was obtained at this concentration of MgCl₂.

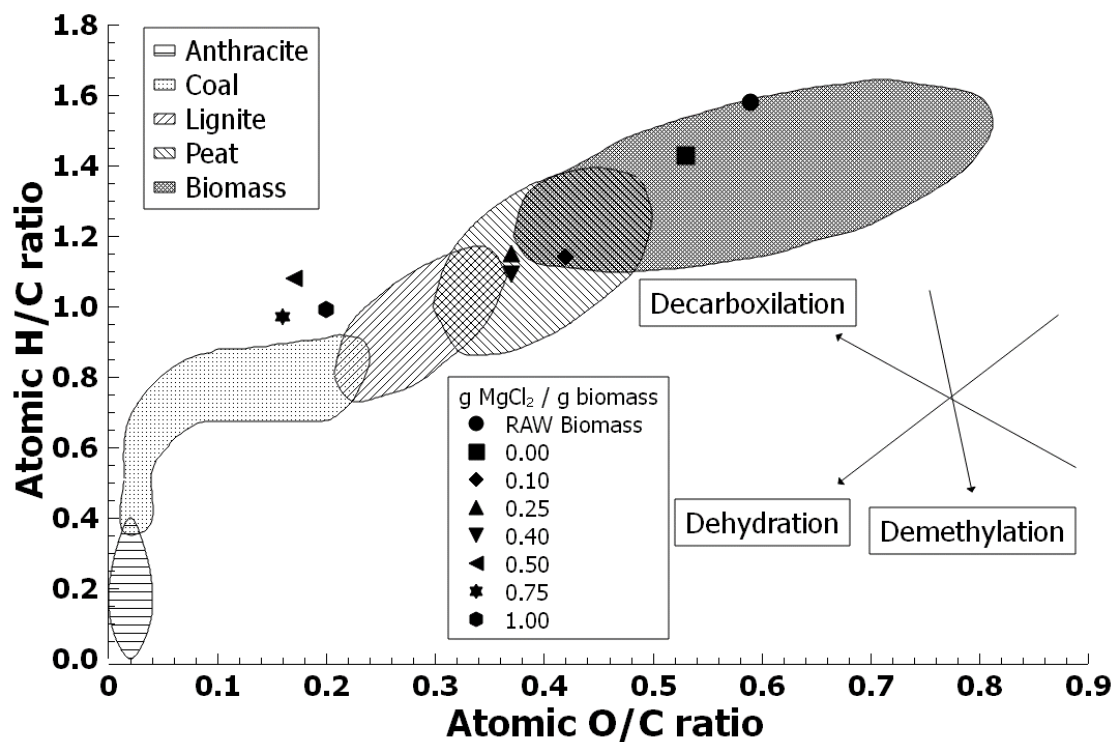


Figure 5. Van Krevelen diagram.

Using the same diagram, it is also possible to predict the reaction(s) that occur during the process, based on the direction from the initial point of the biomass to that of the hydrochar, as shown in Figure 5. In the present study, the path that carbonized biomass has followed shows the same slope as the dehydration reaction. This reaction impacts the components of the biomass, particularly lignin, thus eliminating hydroxyl groups that are present in its structure and, thus, mainly concentrating the carbon content. It is in agreement with the deductions described above.

3.6. Effect of Magnesium Chloride on the Volatile Matter, Ash and Fixed Carbon Content

Table 4 shows the results of the proximate analysis performed on hydrochar that was treated with different doses of magnesium chloride. Volatile matter is reduced with the use of the additive, implying the effective solubilization of a significant portion of the intermediate compounds generated during the HTC process, and that could form part of the hydrochar. The ash content increases mainly due to the effect of the magnesium chloride itself, that might have remained in the hydrochar; this can eventually be corrected by performing a better washing of the hydrochar. Finally, the fixed carbon content increases more than double at higher doses of magnesium chloride, indicating, in general, that the obtained hydrochar has better fuel qualities than untreated biomass.

Table 4. Proximate analysis of the carbonized product.

MgCl ₂ Dose g MgCl ₂ /g Biomass	%Volatile Matter	%Ash	%Fixed Carbon *
0	78.14 ± 0.06	0.03 ± 0.01	21.83
0.1	69.86 ± 0.11	0.39 ± 0.04	29.75
0.25	63.47 ± 0.13	1.22 ± 0.01	35.31
0.4	62.26 ± 0.15	0.54 ± 0.02	37.20
0.5	56.43 ± 0.07	1.76 ± 0.01	41.81
0.75	51.53 ± 0.35	1.18 ± 0.01	47.29
1	50.52 ± 0.32	0.73 ± 0.01	48.76

* Balance.

4. Discussion

Based on the results, the addition of magnesium chloride generates changes in the hydrothermal carbonization process of pine. The process becomes more severe as the dose of the additive increases, but the temperature and time conditions remain the same. It implies that the obtained product is more concentrated in carbon at the cost of a lower mass yield [31], which is what this work demonstrates. This effect is mainly explained by the decomposition of the constituents of lower energy contribution of biomass, such as cellulose and hemicellulose [25]. Additionally, the presence of chloride ions in the solution, resulting from the addition of magnesium chloride, promotes the acid hydrolysis of these constituents [32], explaining the significant difference between the use or not of the additive. The above clearly explains the decrease in mass yield, the increase in HHV, the decrease in elemental oxygen, and the significant concentration of elemental carbon and fixed carbon. It is essential to mention that these results are for *pinus radiata* sawdust, so other biomasses may have different behaviors.

In the particular case of mass performance, experimental set 2 shows an erratic behavior of this parameter. It could be by the polymerization of macromolecules released by the hydrolysis of the constituents of the biomass and that finally are part of the hydrochar [25]. The behavior is not the same in the dose range studied in this work, so future research should study the cause more deeply.

Regarding process scalability, future studies should focus on the application of additives on an industrial scale. The recovery of soluble salts in the liquid fraction generated in HTC and also the recycling flows are considered to be the main strategies for decreasing the cost of operation and its environmental effect [33]. These actions could decrease the gross amount of additive used, making it a more plausible alternative to use.

This study used pure MgCl₂. Nowadays, the industrial application of this additive in the HTC process must be analyzed using minerals enriched with this salt, like bischofite (MgCl₂·6H₂O). This product is obtained from lithium mining and the saltwater desalination process; both are present in the northern region in Chile. The estimated price of bishofite in 2015 is around 155 US\$/ton [34], which makes it capable of adding a new application in the energy biomass conversion process.

5. Conclusions

The best point of operation for the *Pinus radiata* sawdust through the hydrothermal carbonization process was obtained at a temperature of 220 °C and 1 h of residence time, obtaining an energy yield value of 75%.

The addition of magnesium chloride, as an additive in the hydrothermal carbonization of the *pinus radiata* sawdust, shows significant effects in the dose application range of 0.0 to 1.0 g of MgCl₂/g biomass regarding the mass yield of the process.

Within the doses of magnesium chloride studied, it is observed that the best results are obtained at a dose of 0.75 g of MgCl₂/g biomass. The hydrochar has an HHV 32.93% higher than the untreated biomass. Additionally, the use of the additive in this dose generates the early hydrolysis of the constituents of less energy contribution from biomass. It promotes the dehydration reactions that are suffered by the other constituents, generating a hydrochar of remarkable energy properties, with characteristics that are similar to coal according to the Van Krevelen diagram and it has a high fixed carbon content.

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