CHEMICAL ENGINEERING TRANSACTIONS

VOL. 76, 2019

A publication of AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Petar S. Varbanov, Timothy G. Walmsley, Jiří J. Klemeš, Panos Seferlis

ISBN 978-88-95608-73-0; **ISSN** 2283-9216

DOI: 10.3303/CET1976244

Performance Evaluation of Biomass Blends with Additives Treated by Hydrothermal Carbonization

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Hydrothermal carbonization (HTC) is a thermochemical technology of biomass conversion that has some advantages: lower operating temperature than other technologies, ability to process biomass with high moisture content and generation of a final product with a higher calorific value than the original biomass and with hydrophobic characteristics. This study evaluated the influence of temperature, time, biomass blend, nature and dose of additive in the HTC process. The response variables were mass yield (MY) and higher heating value (HHV), generating a total of 128 experiments that were grouped in 8 complete factorial designs (2^4). Pressed olive (OLV), oat husks (AV), Pinus radiata sawdust (AS), and raps seeds (RPS) were used as raw biomass. MY and HHV had an R^2 above 0.90 using the response equations of Experimental Design. Results indicate that temperature was the main effect in both responses, since it produced a decrease of MY between 5 and 10 %, and an increase of HHV between 1.5 and 2.2 MJ / kg. Use of additives did not significantly improve the energy yield. On the other hand, addition of a 'more reactive' biomass with increasing temperature achieved an important improvement in the HHV value. It is a positive fact because the studied biomass presents strong seasonal and geographical availability.

1. Introduction

One of the main goals of the waste-to-energy technologies is to convert the current world stage of energy production into a sustainable process (Lynam et al., 2015), using waste materials (agricultural waste, food waste, among others) as raw materials. In the developing countries, there is a high dependence on the extraction of 'commodities', which is why a change to a productive matrix based on renewable resources is necessary (Ong et al., 2018), among them the 'bioenergy', an energy that is generated from biomass (Reza et al., 2013). An important alternative for the conversion and treatment of the biomass is the hydrothermal carbonization (HTC) (Darmawan et al., 2018), which constitutes a process of energetic densification of the raw biomass (Wang et al., 2018). The solid obtained has a higher calorific value, hydrophobic properties and greater ease of transport and storage (Li et al., 2015). A relatively low temperature required during the process, compared to other organic waste conversion techniques, and its ability to work with biomass with a high moisture content are the strongest points of this method (Román et al., 2018).

During the past decade, the objective of the HTC studies has focused mainly on the identification of appropriate biomasses for conversion to hydrochar, with an economic approach (abundance, ease of transportation and storage) (Titirici and Antonietti, 2009) and an energetic approach (mass yield and energy yield) (Wang et al., 2018). The next challenge of the HTC process is to achieve high yields on a full scale. Due to this, it is necessary to develop studies that provide knowledge about the behavior of the biomass in different operating conditions of the process, but above all its energy yield should be evaluated in the presence of additives that could improve its carbonization and its degree of interaction in biomass blends. The importance of using blends is to counteract the high variability in the composition of the biomass and its seasonal and geographical availability, this is a key factor in its feasibility of use in the future (Lynam et al., 2012).

Paper Received: 15/03/2019; Revised: 12/04/2019; Accepted: 15/04/2019
Please cite this article as: Vallejo F., Diaz-Robles L.A., Cubillos F., Vega R., Gomez J., Pino-Cortes E., Bascunan B., Carcamo P., Parra F., Urzua A., Carrasco S., 2019, Performance Evaluation of Biomass Blends with Additives Treated by Hydrothermal Carbonization, Chemical Engineering Transactions, 76, 1459-1464 DOI:10.3303/CET1976244

Currently, the HTC process is being researched to maximize energy yield and to improve the properties of the product as ash percentage and calorific value. Various salts have been proposed before, for example, calcium chloride, magnesium lactate, sodium chloride, and lithium chloride, among others (Lynam et al., 2011). The results indicate that there is an improvement in the energy yield and in the HHV of the hydrochar compared to the carbonizations without an additive. However, the amounts that are recommended to be added and that are in the range of 1 g of additive per g of dry biomass make the search for the additive controlled by its cost. In developing countries, many of the salts that have been investigated have high prices, which makes it impractical to use them at full scale. Magnesium chloride ($MgCl_2$) and lithium chloride presents similar physicochemical characteristics, and $MgCl_2$ price is lower; while peracetic acid has shown to transform the chains of polysaccharides that bind biomass (hemicellulose, lignin, and cellulose) into its elementary monomers, which would benefit the reaction of hydrothermal carbonization (Wang et al., 2018). The present work proposes an analysis by an experimental design of 4 factors in 2 levels for the study of the influence of time and temperature of the process, the change of biomass in eight blends and the addition of $MgCl_2$ and peracetic acid during the process HTC in the reactor.

2. Materials and methods

2.1 Biomass

Olive pressed (OLV), radiata pine sawdust (AS), raps seed (RPS) and oat skin (AV) were used in the experiments reported in this paper. These biomasses were obtained in Temuco and Gorbea, both cities in southern Chile during the year 2016. They were stored and used as received. The determination of the moisture (M) was performed with the gravimetric method and the HHV was carried out in a Parr 6200 calorimeter. Proximate analysis was performed by the Van Soest method (Lynam et al., 2015) of NDF-ADF-ADL (neutral detergent fiber, acid detergent fiber, and acid detergent lignin), the main fractions are the ash, lignin, cellulose, hemicellulose and aqueous extractives (A, L, C, H and AE, respectively). Also, the raw biomass was analyzed in terms of C, H, N and O mass fractions. Table 1 shows the full characterization for each biomass.

Table 1: Raw biomasses characterization

Biomass	M (%)	Proximate analysis					HHV	Ultimate analysis			
		A (%)	L (%)	C (%)	H (%)	AE (%)	(MJ/kg)	C (%)	H (%)	N (%)	O (%)
AS	7.44	0.21	30.0	42.0	25.0	2.79	20.11	51.911	6.898	0.065	40.815
AV	7.35	4.44	12.9	37.6	23.3	21.8	18.66	46.771	7.250	0.490	40.767
RPS	7.26	6.25	36.3	10.3	35.3	11.9	21.34	51.682	6.967	4.973	29.428
OLV	8.20	11.9	14.2	24.1	11.0	38.8	20.57	49.268	4.592	1.925	31.690

2.2 Hydrothermal carbonization

Hydrothermal carbonization was carried out in a reactor with stirring, of high pressure and temperature, model HiPR-SF5L with a capacity of 5 L. The reactor has a heating surface and a thermocouple to measure the temperature inside of the reactor. The pressure value set was higher than the calculated vapor pressure at wall temperature measured by a thermocouple. The inlet and outlet of water were controlled through a butterfly valve. An amount of 240 g of the biomass mixture was charged with the weight composition described in Experimental design section. Nitrogen was introduced by a valve system to remove the air present in the reactor chamber. All runs were made with biomass: water ratio of 1:12 and an agitation of 108 rpm. Anhydrous magnesium chloride (USP, purity > 99 %, powdered) and peracetic acid (15 wt. %) were purchased from a local Chilean supplier.

2.3 Experimental design

The influence of temperature (T), time (t), biomass blend type (B), and nature and dose of additive (D) on mass yield (MY) and higher heating value (HHV) was studied with an experimental design. The experimental design of these five factors can be expressed as $[2^4 * 8^1]$. Table 2 indicates the levels of the factors used. The execution of the experimental design proposed generated 128 experiments, performed in duplicate. Biomass blends were prepared by maintaining main biomass (70 %) fixed and changing the secondary biomass (30 %). Thus, to make easy the further analysis of the results, Table 3 shows the 8 experimental sets that were considered. Each set allowed to determinate the influence of the factors on each biomass, i.e. how the temperature, time, secondary biomass added, and additive nature and dose change the MY and the HHV of the main biomass. Sets 1 – 4 grouped the runs with $MgCl_2$ and sets 5 – 8 for the runs with peracetic acid.

Table 2: Factors and levels in experimental design

Factors	Units	Levels			
Temperature	ºC	-1: 175		+1: 225	
Time	min	-1: 30		+1: 60	
Biomass blend	----------	M1: OLV – AS	M2: OLV – AV	M3: RPS – AS	M4: RPS – AV
		M5: AV – AS	M6: AV – RPS	M7: AS – RPS	M8: AS – OLV
Additive nature	----------	$MgCl_2$		Peracetic acid	
Additive dose	g/g biomass	-1: 0		+1: 1	

Table 3: Experimental sets for analysis

SET	T		t		B		D	
1	175	225	30	60	OLV-AS	OLV-AS	w.o. additive	$1\ \frac{g\ MgCl_2}{g\ db}$
2					RPS – AS	RPS – AV		
3					AV – AS	AV – RPS		
4					AS – RPS	AS – OLV		
5					OLV – AS	OLV – AV		$1\ \frac{mL\ MgCl_2}{g\ db}$
6					RPS – AS	RPS – AV		
7					AV – AS	AV – RPS		
8					AS – RPS	AS – OLV		

In each experiment, mass yield (MY), hydrochar higher heating value (HHV) and energy yield (EY) were determined as shown in Eq(1) and Eq(2).

$$MY=\frac{\text{Dry hydrochar mass}}{\text{Dry raw biomass mass}}\times 100\ \% \qquad (1)$$

$$EY=MY\times\frac{\text{Hydrochar HHV}}{\text{Raw biomass HHV}} \qquad (2)$$

3. Results and discussion

3.1 Characterization of biomass blends

As indicated above, Table 1 presents the characterization of the raw biomass. MY measures the degradation of biomass macromolecules (i. e. hemicellulose, cellulose, and lignin) during the HTC process. Hemicellulose and the aqueous extractives are the first to leave the structure of the biomass (150 - 180 ºC), followed by hemicellulose (180 - 230 ºC) and cellulose (> 200 ºC). Lignin is usually considered inert in the usual ranges of operation of HTC, but there is no conclusive evidence for this assumption (Reza et al., 2013). In general, these temperature ranges are only referential because they depend on the composition and type of biomass (Jung and Kruse, 2017), and this explains the difficulty of finding mathematical relationships that are applicable to different types of biomass and blends (Jung and Kruse, 2017). However, a novel concept could be applied for the analysis, which defines the "reactive part" of the biomass as the sum of AE and hemicellulose, and as "non-reactive part" (or inert) as the sum of the ashes and lignin (Lynam et al., 2015). Table 4 shows the characteristics of all blends used. This additional characterization is of utmost importance since the value of the HHV and the ashes of each biomass blends do not correspond to a linear relationship with respect to their individual values.

3.2 Analysis of experimental design

The importance of the experimental design lies in the possibility of quantifying the effect of each variable on the response (Montgomery and Runger, 2003). The significant effects were calculated by considering the High Order Effects and with 95 % confidence. Thus, an effect was significant if its value met with the condition indicated in the Eq(3). Where, Ef is the effect value, t is the Student's two-tailed test value for α = 0.025, v=15 (t = 2.131) and s is the calculated variance with high order effects (Triola, 2004). The software used for statistical analysis was XLSTAT (Addinsoft, 2019).

$$Ef \geq t \times s \qquad (3)$$

Table 4: HHV and ash of raw biomass

	OLV-AS	OLV-AV	RPS-AS	RPS-AV	AV-AS	AV-RPS	AS-RPS	AS-OLV
HHV (MJ/kg)	21.5	20.8	20.7	20.2	19.5	19.6	20.5	20.9
Ash (%)	2.61	0.37	4.67	5.67	3.17	5.00	1.56	1.83

Temperature was the main effect (higher effect value) in both responses, and only in the MY of sets 5 and 6 another variable had a higher effect, as shown in Tables 5 and 6. The increase of T generated a decrease in MY and an increase in HHV. The change in biomass was another important effect. In the experimental design, the biomass blend was a qualitative factor, the added biomass had a higher reactive portion in one of the levels used (coded with +1). The observed effect was a decrease in the MY and an increase of the HHV value in all the cases which this variable was significant. The use of additive presented a variable influence, runs with $MgCl_2$ show a decrease of the HHV in all cases, which was not desired. On the other hand, the MY of set 2 increased and MY of set 4 decreased with the use of additives. Time was significant in the MY of sets 1 and 3 with a decrease in response while producing an increase in the HHV of the sets 5-8. In terms of interactions, there were clear trends, for example, T x D, which was significant for all blends with $MgCl_2$ (sets 1-4), and always had the same sign of T, indicating the strong dependency relationship towards that variable. The interaction D x B was significant only once in MY of set 1 and the interactions of time with the other variables were not significant in any case. Moreover, the so-called 'reactive part' of biomass, i.e. sum of hemicellulose and aqueous extractives, allowed to explain to a large extent the results obtained, e. g. with the olive (50 % reactive) and the raps (47 %), a lower mass yield than sawdust blends (28 %) was obtained, because of a greater degradation and solubilization in the aqueous medium.

The DoE analysis for runs with $MgCl_2$ is presented in Table 5. The added biomass (BA) is indicated according to the experimental design and the response equation for the MY and the HHV is shown. The adjustment of the prediction to the experimental values, measured with the R^2, indicates that the equations are valid and allow to predict with reasonable confidence both response variable because the R^2 widely exceeds 0.92, except the case of the HVH of AS-OLV that had 0.88. The DoE analysis for the runs with peracetic acid is presented in Table 6. Like with addition of $MgCl_2$, prediction to the experimental values, measured with the R^2, indicates that the equations are valid and allow to predict with reasonable confidence both response variable because the R^2 was more than 0.92 for all cases.

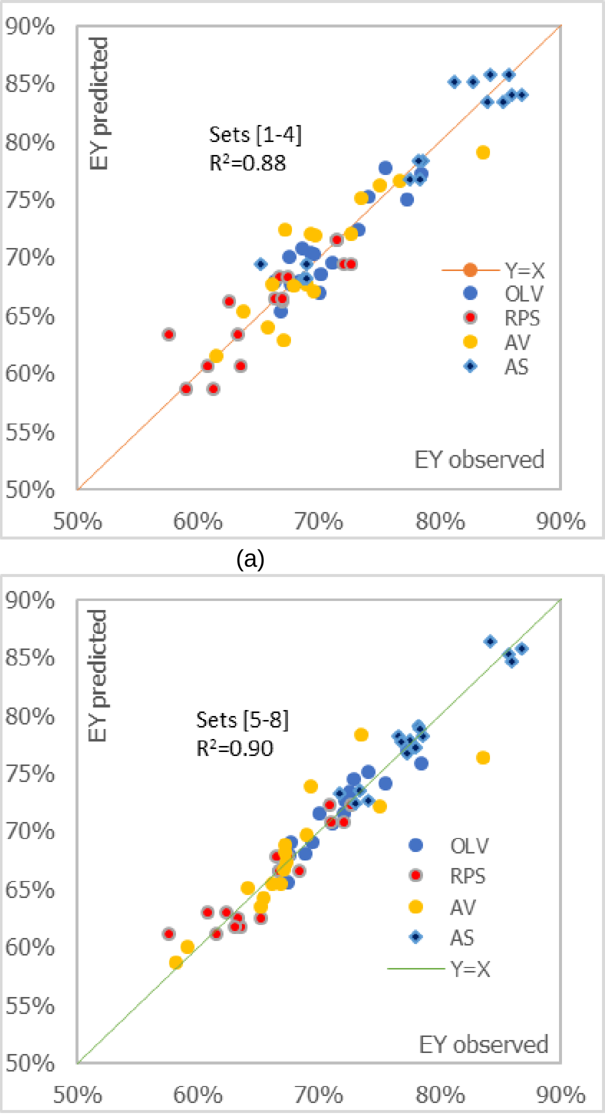
Table 5: Experimental design and coefficients obtained for the significant effects. Runs with $MgCl_2$

MB	BA		RV	Response relation	R^2
OLV	–1	AS	MY	$61.44 – 4.85X_T – 3.09X_B – 1.71X_TX_D + 1.16X_BX_D – 1.02X_t$	0.96
	+1	AV	HHV	$24.54 + 1.70X_T – 0.48X_D + 0.435X_TX_D$	0.97
RPS	–1	AS	MY	$54.33 – 5.80X_T – 4.24X_B – 1.76X_TX_D + 1.41X_D$	0.95
	+1	AV	HHV	$24.95 + 1.85X_T – 0.50X_D + 0.4X_B + 0.27X_TX_D$	0.98
AV	–1	AS	MY	$65.19 – 6.72X_T – 3.08X_B – 2.00X_t + 1.74X_TX_D$	0.92
	+1	RPS	HHV	$21.20 + 2.15X_T + 0.52X_TX_D – 0.51 X_D + 0.50X_B$	0.97
AS	–1	RPS	MY	$73.70 – 10.09X_T – 3.36X_TX_D – 1.72X_D$	0.97
	+1	OLV	HHV	$22.37 + 1.47X_T + 0.48X_TX_D$	0.88

Analysis of response equations in Table 5 and 6 indicated for the MY, an increase in the temperature from 175 to 225 ºC produced a decrease of at least 5 % in the case of OLV blends, and up to 10 % in AS blends, an expected trend because AS and OLV were the biomasses with the lowest and most reactive, respectively. Olive and sawdust had 11 and 25 % of hemicellulose, respectively. The higher value of hemicellulose in sawdust caused a greater variability in the biomass change effect. On the other hand, RPS had the lowest cellulose and the highest hemicellulose values and its blends had a lower average value, 54.33 %. At the other extreme, AS blends had 73.70 %. Another significant effect in the MY is the change of biomass (30 wt. %), in the blends of OLV, RPS and AV obtaining an impact in the response of between +0.5 to -4.2 %. The interaction T x AD was significant for all biomasses, and for the RPS and the AS was also the additive. The time, except for the OLV, did not prove to be a significant effect. For the HTC runs with peracetic acid the results obtained showed similar behaviour. AS blends had the highest MY and the RPS ones the lowest. However, as indicated in Table 6 a lower MY was observed, i. e. the acid worked better than $MgCl_2$ in decrease the MY, which is similar to the results reported by Lynam et al. (2012), and may be due to a greater decomposition of cellulose in the reaction. For sets 1-4, a temperature increase effect on the HHV is positive in all cases, with values of 1.47 to 2.15 MJ/kg, for mixtures of AS and AV, respectively. The average values vary from 21.20 to 24.95 MJ/kg, for AV and RPS, respectively. The trend shown in Table 1 was very similar, with a higher value of HHV of RPS and the lowest value is for AV.

Table 6: Experimental design and coefficients obtained for the significant effects. Runs with peracetic acid.

MB	BA		RV	Response relation	R^2
OLV	–1	AS	MY	$60.95 - 3.01X_T - 3.73X_B + 0.91X_TX_B - 0.67X_D$	0.96
	+1	AV	HHV	$24.86 + 1.29X_T + 0.11X_B + 0.18X_t - 0.16X_D$	0.99
RPS	–1	AS	MY	$53.33 - 4.32X_B - 4.04X_T + 1.32X_TX_B$	0.96
	+1	AV	HHV	$25.36 + 1.55X_T + 0.32X_B + 0.25\ X_t$	0.98
AV	–1	AS	MY	$60.82 - 5.35X_T - 4.18X_D - 3.26\ X_B + 3.12X_TX_D$	0.91
	+1	RPS	HHV	$21.97 + 1.69X_T + 0.64X_B + 0.28X_TX_B + 0.27X_D + 0.25X_t$	0.99
AS	–1	RPS	MY	$71.74 - 5.95X_T - 3.68X_D - 0.70X_t + 0.51X_B + 0.78X_TX_D$	0.98
	+1	OLV	HHV	$22.77 + 1.05X_T + 0.18X_D + 0.15X_t$	0.99



(a)

(b)

Figure 1. Predicted and observed EY for sets, (a) HTC runs with $MgCl_2$ (b) HTC runs with peracetic acid

On the other hand, the HHV of the mixtures with peracetic acid (sets 5-8) show a higher average value, due to the change described in the MY that indicates a greater degradation in the biomass, i.e. oxygen and hydrogen decreased, and carbon increased in the elemental composition. However, as other authors have already described, the EY does not present modifications when changing the additive (Lynam, et al., 2011). Figure 1 indicates that the AS blends were those that retain the greatest amount of energy from the original biomass. As explained before, the higher content of cellulose and lignin (72 %) prevents an EY decrease. EY was calculated with Eq(2), where MY and HHV were the predicted values. The adjustment measured with R^2 was 0.88 (sets 1-

4) and 0.90 (sets 5-8). To ensure a value greater than 80 % in EY, mixtures of AS + RPS at a temperature of 175ºC are recommended. On the other hand, the highest HHV were obtained for RPS + AV mixtures without additives and at 225 ºC. From this analysis, MY was more significant that HHV on EY determination.

4. Conclusions

The evaluation of several variables in the HTC process by Experimental Design allowed to predict the values of MY and HHV in the study region. The analysis performed indicates that the temperature and the blend type were the main factors, discarding the possible influence of the nature and doses of additives in the improvement of the process. An increase in the temperature produced a decrease of MY between 5 and 10 %, and an increase of the HHV between 1.5 and 2.2 MJ/kg. The addition of a biomass with a greater reactive part (eg, RPS + AS-AV, set 6) produced a similar effect in the MY and HHV, this fact is very important because biomass has a geographical and seasonal availability. Finally, the reaction time between 0.5 and 1 h did not show a significant effect.

Further studies must be carried out to optimize the blend composition. Also, the highest ash content of olive and oats, both agricultural residues, must be considered since the ashes does not react within the HTC process and that decreases the calorific value.

Acknowledgments

This work has been founded by Projects FONDEF Idea ID15I10580 and BMBF-CONICYT 150067.

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