CONVERTING SOLID WASTE FROM ABATTOIRS INTO HYDROCHAR

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1.0 EXECUTIVE SUMMARY

Paunch waste and DAF sludge were sampled and characterized before being converted to hydrochar. Six different hydrochars were produced and characterized. Each hydrochar was then assessed for in terms of:

- Value as an agricultural fertilizer using pot trials and soil enzyme assays
- Energetic value

The results of the laboratory experiments indicate that conversion of paunch waste and a mix of paunch waste and DAF sludge into hydrochar is a promising alternative to the conventional practice of composting. Hydrothermal carbonization is a thermochemical process which reduced the volume and mass of these waste streams. When assessed for agronomic value, these hydrochars led to a 20% increase in wheat yield compared to the compost. On the other hand, hydrochar from DAF sludge alone had no effect on wheat yield compared to the compost and yielded a product with unsuitable characteristics.

Our study has identified the most suitable type (paunch waste or composted paunch waste and manure) of feedstock for hydrothermal carbonization. Temperature of carbonization was not a significant parameter to determine the quality of the product. In order to bring this project to the next stage (construction of a pilot plant for demonstration) it would be necessary to:

- Assess the different markets for hydrochars. At the moment, agricultural use and material for combustion has been assessed, but other uses such as remediation of polluted areas have not been investigated. It is also uncertain the optimal dose of hydrochar application.
- Evaluate other thermochemical conversion alternatives, including supercritical water gasification.

2.0 INTRODUCTION

Meat processing industries face many challenges in relation to solid waste management. As an example, improper storage of waste can result in soil and water contamination. Atmospheric contamination can also result from dust or odors. Moreover, greenhouse gases are produced during the treatment and transport of solids.

Best practices aim to avoid and reduce the amount of solid waste generated and, when there is no other alternative, to reuse or recycle the waste.

Most of the solid waste produced by the meat processing industry are organic and present the following characteristics: Very high moisture content, nutrient-rich and presence of microorganisms (including pathogens). Examples of organic solid waste include manure, paunch and gut contents and biological sludges from wastewater treatment. Manure is originated by animals, but also, includes some times human wastes, as due to their location, meat processing plants are not always connected to the municipal sewerage system.

At present, the management of solid waste in Australian meat processing industries includes composting, vermicomposting, anaerobic lagoons and ensilage. Composting is the most widespread technique to treat the organic solid wastes in the Australian meat processing industry.

Cattle paunches are the major source of solid wastes from meat processing plants. Each year a large abattoir can produce more than 3,000 tonnes of paunch and spend over 17 dollars per tonne for its disposal. Theoretically, it could be possible to transform this product in a fertilizer, but in practice the cost of doing so exceeds the value of the product. However, composting has been recommended as the best practice for this kind of waste (Wilson, 1992).

In other regions of the world, waste to energy technologies are used to produce energy from meat industry wastes. The use of biomass in this way reduces the costs associated with its disposal (which has been prohibited in many locations by strict regulations). This reduction in cost is achieved by diminishing the weight and volume of these wastes, energy recovery and lower toxic gas emissions when compared to fossil fuels. However, in Australia, the relatively low energy costs have prevented a wider adoption of these techniques. There is a potential of these technologies to be adopted if energy generation is coupled with the production of useful by-products.

Pyrolysis is a thermochemical technique offering several advantages: No emission of greenhouse gases, elimination of odors and reducing the amount of residues. An interesting feature of pyrolysis is the production of both energy and a form of charcoal intended for soil amendment and known as biochar. Thus, biochar is a solid, carbonaceous and porous material that can be recycled into the soil with benefits for soil quality and, as a consequence, soil fertility.

In the last years, there have been attempts to improve the management of solid waste in the meat industry. This has included not only the use of fast and slow pyrolysis (AMPC project A.ENV.0101, AMPC project A.ENV.0111) but also torrefaction (project 2013/5015) to treat paunch waste. However, these pyrolysis methods are not optimum for the treatment of wet feedstocks, such as paunch and other alternatives should be explored. Conventional pyrolysis requires the feedstock to be reasonably dry and this implies an additional cost that renders the process uneconomical. Similarly, torrefaction (known also as mild pyrolysis) faces the problem of the usage of energy to evaporate the water present in the moisture, rendering it uneconomic.

Thus, the feedstocks used in torrefaction have a maximum moisture content of 15 % (Acharya et al., 2012) and, in this way, torrefaction has only proved to be economic when woody feedstocks are used (Batidzirai et al., 2013). In contrast, hydrothermal carbonization does not require the biomass input to be dried, resulting in a more favorable energetic balance.

Hydrothermal carbonization is carried out in aqueous conditions at a temperature range of 180-250 ºC and pressure. Thus, and in contrast with torrefaction, biomass does not have to be dried by means of energy-consuming processes. Using hydrothermal carbonization, there is a process of mechanical dewatering and thus, unlike in torrefaction, water does not have to be evaporated. Hydrothermal carbonization, unlike torrefaction allows to process feedstocks having up to 90 % moisture (Hitzl et al., in press).

Lately, there has been an increasing interest in hydrothermal carbonization. This technique has been recently developed in Europe and, at present, is not used in commercial or experimental plants in Australia. Hydrothermal carbonization has the advantage that wet feedstocks can be processed and could be more suitable than common pyrolysis for the meat process industry in terms of energy gains. Hydrothermal carbonization reduces the energy input required to treat wet solid waste in comparison to other pyrolytic technologies and delivers more amount of solid product. The solid product (hydrochar) is a high-energy product that can be used as a fuel (Kalderis et al., 2014) but it could have a similar potential to biochar to increase soil fertility. Although there are plenty of references documenting the positive effects of biochar on soil properties (Lehmann et al., 2007; Cely et al., 2015; Cely et al; 2014; Liu et al; 2013; Mendez et al., 2014; Sohi, 2012), however, there is much more uncertainty concerning the potential benefits of hydrochars to agricultural soils and this gap of knowledge should be addressed. Hydrochar research with respect to its use as soil amendment is still on its infancy. Even if not applied to the soil, hydrochar has a high calorific power (Hitzl et al., in press) and the process water obtained from hydrothermal carbonization can be used to irrigate the land (Hitzl et al., in press).

The properties of hydrochar and its suitability to be used in different types of soils depend on the temperature of preparation. Thus, it is necessary to characterize hydrochars at different temperatures in order to optimize the production of by-products associated to the waste to energy conversion process.

It is well established that the biological component of a soil is a key issue in processes such as nutrient cycling or organic matter transformations. Soil biochemical properties, and, in particular soil enzymes, anticipate changes in soil quality. Thus they have been used as indicators of soil quality in a variety of situations (Paz-Ferreiro et al., in press). Soil biological properties are sensitive to the presence of pollutants in the soil (Paz-Ferreiro and Fu, in press). However, the effects of hydrochars on soil biological properties of agricultural soils have not been reported. Thus we rely on the hypothesis that potential impacts of hydrochar on soil quality and on environment can be assessed by soil quality and by soil biodiversity indices derived from soil biochemical properties. Therefore, this proposal also intends to achieve a process-based understanding of hydrochar–soil interactions and to assess the impact of these interactions on soil biodiversity and on key soil properties related to biological processes.

3.0 PROJECT OBJECTIVES

The overarching aim of the project was to:

1. Determine the chemical composition, physical properties and thermal behavior of:
    - (i) Paunch waste
    - (ii) DAF sludge
    - (iii) Composted paunch waste and manure
2. Prepare different hydrochars from paunch waste and characterize each hydrochar in terms of:
    - (iv) Chemical composition
    - (v) Physical properties
    - (vi) Thermal Behavior
3. Assess the fertilizer value of the hydrochars
    - (vii) Pot trial assessing the effect of applying hydrochars upon wheat yield
    - (viii) Soil enzyme assays to examine changes in soil biochemistry when hydrochar is applied as a fertilizer.
4. Assess the energetic value of the hydrochars
    - (ix) Calorific value of hydrochar for use as a solid fuel

4.0 METHODOLOGY

4.1 Sample collection and characterization

On the 2nd of June 2016, samples were collected from Thomas Foods International processing facility in Murray Bridge, South Australia. Paunch waste, DAF sludge and a mixture of paunch waste, DAF sludge and manure were collected and brought back to RMIT University.

4.2. Hydrochar production and characterization

The hydrochars were produced as follows. 1.2L of waste material (50g dry waste/L) was placed in a Teflon vessel. The vessel was inserted in to a 2 L hastelloy pressure reactor (www.demede.es) and then the reactor was purged with nitrogen gas. An electric heater was used to supply the heat to maintain the temperature of the reactor. The reactor was then heated to the desired treatment temperature set using a PID controller. The reactor pressure was monitored but not controlled during the heating. When the desired temperature was reached inside the reactor, the 6 h residence time was initiated.

Once 6hrs of residence time elapsed, heating ceased and the reactor was cooled to room temperature. The final solution was filtered and the remaining solid residue was washed with 1L of distilled water. Following washing, the solid was dried at 60°C for 24hours. Hydrochar yield was calculated by the final dry weigh and the initial dry waste in the solution

pH and electrical conductivity (EC) was determined in a ratio soil:water 1:2.5 (g mL^{-1}), cation exchange capacity (CEC) was determined using the ammonium acetate method at pH7.0 , Total organic matter (TOM) and total organic carbon (TOC) was determined by the dry combustion method at 540°C and metal content will be determined using atomic absorption spectrophotometer after sample extraction by digestion with 3:1 (v/v) concentrated HCl/HNO3.

Each hydrochar was subjected to thermogravimetric (TG), derivative thermogravimetric (dTG) and differential thermal analysis (DTA) in a thermobalance Labsys Setaram. Specifically, around 80 mg of each sample was heated at 15°C min-1 to 850°C in air atmosphere using a flow rate of 30 mL min^{-1}.

The BET surface area of each hydrochar was determined using nitrogen adsorption analysis at 77K using a Micrometrics ASAP 2420. Pore properties were determined using a Micrometrics AutoPore IV 9500. Fixed C content, ash and volatile fraction of each hydrochar was determined by thermogravimetry. Briefly, samples were heated up to a temperature of 900°C under a N_2 atmosphere at a flux of 40 mL min^{-1}. Volatile fraction was determined as the weight loss from 150°C to 900°C under nitrogen atmosphere and fixed C as the weight produced when the final sample was burnt under an air atmosphere. At 900°C, air is introduced until a constant weight is reached and ash is determined as the final weight of the samples.

4.3. Soil collection and characterization

Around 10kg of soil was collected and sieved to 2mm before being analyzed for soil texture, pH and EC, TOM, cation exchange capacity, trace metal content, N, P and K content.

4.4. Pot trial

The potential of using hydrochar to improve wheat yield was assessed by way of a pot trial. After sieving to 2mm, the soil was transferred in to plastic pots and wheat was planted at a rate of 200kg ha^{-1}. Each hydrochar was added at a rate of 3% of the total soil weight. Compost was added to the soil at the same rate as the hydrochar and this was used as the control in the experiment. In total there were six different hydrochar treatments plus the control, which were replicated four times. After 74 days of growing time the wheat biomass was harvested and oven dried to determine the yield. Data were analyzed used a one-way ANOVA.

4.5. Soil enzyme activities

Enzyme assays are simple, rapid and sensitive to land use changes. There are many ways to measure soil quality. When examining the effect of adding amendments, changes in physical and chemical properties may take several months to be recognized.

Over the past ten years, soil biochemical properties have received attention as a more appropriate measure of soil quality when the effect of amendments is in question. These properties are determined by microbial reactions involved in nutrient cycling and are highly responsive to management changes, for example the application of an amendment (Paz-Ferreiro & Fu 2016).

The activities of the following enzymes were measured 72 days post treatment for all treatments, including the compost treated control.

// Dehydrogenase activity in soil represents the activities of microbes responsible for the oxidation of organic molecules during microbial respiration. It has been used as a measure of overall activity of microorganisms in soil.

// Phosphomonoesterase activity represents important microbial functions around P cycling in soil. Specifically this enzyme is known to catalyze the hydrolysis of phosphomonoesters in to orthophosphates, which are available for plant uptake.

// β-glucosidase is involved in C cycling in soil. Specifically β-glucosidase is involved in the breakdown of cellose by hydrolyzing the degradation products of cellulase.
Phosphodiesterase is involved P cycling. Specifically, by catalyzing reactions which lead to the formation of available phosphates in soil.

5.0 PROJECT OUTCOMES

The progress of the project has been according to contract, with RMIT University producing 6 instead of the 5 hydrochars mentioned in the agreement. The hydrochars were produced in Spain and this created more issues than expected around importing the hydrochars in to Australia. This delayed the project for around six months. RMIT University is commissioning its own hydrothermal carbonization facility, which would allow future projects to be completely carried out at our facilities.

In spite of the delays and the additional effort in terms of analyses, the project was kept within the allocated budget.

6.0 DISCUSSION

6.1 Hydrochar production and characterization

Six hydrochars and their corresponding yields are presented in table 1. In the context of waste management, hydrochar produced from paunch at 240°C had a yield of 49.5%, which indicates that the waste stream could be halved via hydrothermal carbonization. This effect was less so (56.2%) at the lower production temperature (180°C). Similarly, for the DAF sludge, the yield was lower (59.5% for 240°C) compared to 67.5% when 180°C was the temperature of production.

For the DAF sludge, the temperature had no effect on yield (75.2%), suggesting that it is more resistant to thermochemical degradation at these temperatures compared to the paunch material.

These differences in yield can be explained with reference to the thermal properties of the hydrochars. Mass loss involves the release of volatiles from the feedstock, as the temperature of production increased from 180 to 240°C, hydrochar yield varied due to differences in the chemical composition of the feedstock. Specifically, at the lower temperature of production more volatile matter was maintained during carbonization, leading to a higher yield. At the higher temperature of production more volatile matter was released, resulting in a lower product yield. An increase in fixed carbon with an increase in production temperature can be attributed to this devolatilisation of volatile matter. In both cases though, the loss in volatile matter was lower than the increase in fixed carbon, suggesting that some volatile matter was released during carbonization and was not converted to fixed carbon in the output hydrochars.

Paunch waste hydrochars had relatively low ash content (2.1 and 2.8% at 180 and 240°C respectively) compared to the mix hydrochars (41.9 and 43.2% at 180 and 240°C respectively). Generally, the ash component tends to be nutrient rich (Wang, Camps-Arbestain & Hedley 2014) , which infers that the produced hydrochars range in value as an agricultural fertilizer. Within feedstock, the different temperature of production may also influence the availability of such nutrients when applied as a soil amendment. For example phosphorus tends to be more available when higher temperatures of carbonization are used (Wang et al. 2012).

The surface areas of the materials were relatively low compared to other char materials (biochars). While this would not pose an impediment for agronomic purposes, it would be necessary to pre-treat the treatment and increase the surface area if the material was to be commercialized as an adsorbent for organic contaminants. It was not possible to estimate surface area values for DAF sludge hydrochar due to its viscous characteristics.

pH and EC values and nutrient contents suggested that the materials would have an application as soil conditioner.

6.2. Incubation experiments

Soil was collected from a grazing paddock near Bendigo, Victoria and characterized as loamy sand. The region has a mean annual rainfall of 514mm/yr (BOM 2017). The soil was air dried and sieved to 2mm for characterization and use in the wheat growing experiment. Several characteristics of the soil are presented in table 3. The soil was acidic with pH of 5.71 and relatively low conductivity (226 µS cm-1). The soil was in high organic content (10.42% by weight).

The wheat yield is presented in table 4 below. Yield is expressed in grams of dried biomass.
Four of the amendments led to an increase in wheat yield (PAUNCH180, PAUNCH 240, MIX180 and MIX240). The magnitude of the increase did not vary according to amendment type ($p>0.05$); the yield increased 1.2 times more than the control for these four treatments. The DAF amendments had no effect on wheat yield compared to the control.

Hydrochars produced from both paunch and a mixture of paunch and DAF sludge led to a significant and marked increase in wheat yield in comparison to the compost. This suggests that the conversion of paunch and a mix of paunch and DAF to hydrochar presents an opportunity to add value to these waste streams, which would otherwise be composted.

The results of the soil enzyme assays are presented in table 5 below.

Dehydrogenase activity was increased by two amendments. PAUNCH240 led to a twofold increase in dehydrogenase activity compared to the control (p<0.05). The MIX240 amendment had the greatest effect (3.3 times higher than the control) (p<0.05). Dehydrogenase activity were unaffected by the other amendments (p>0.05). Dehydrogenase activity is a measure of overall microbial activity in soil; this is because it is an intracellular enzyme involved in microbial respiration amongst all microorganisms thus it is considered a suitable indicator of soil quality and microbial activity (Paz-Ferreiro et al. 2012). The results indicate that hydrochars produced at 240°C enhanced the efficiency of microorganisms compared to hydrochars produced at 180°C, which had no effect compared to the control.

Phosphomonoesterase activity was unaffected by all but one amendment; MIX240 decreased phosphomonoesterase activity by 2.6 times compared to the control. This decrease proves difficult to explain as generally the addition of organic amendments leads to an increase in phosphatase activity. Given the relatively high ash content of MIX240 coupled to a higher temperature of production, it is reasonable to suggest that P may be more available compared to the other amendments. The decrease in phosphatase activity could be due to a reduced demand for P cycling (from inorganic P to organic P), as the addition of MIX240 may have supplied the largest amounts of readily available P.

Phosphodiesterase activity was increased by the paunch and mix of paunch and DAF sludge hydrochars. Specifically PAUNCH180 and PAUNCH240 increased phosphodiesterase activity by 1.5 and 1.2 times that observed in the control. This increase was more pronounced in the hydrochars produced from a mix of paunch and DAF sludge (1.9 and 2.5 times more than the control for MIX180 and MIX240 respectively). In the case of the PAUNCH amendments, the increase in phosphodiesterase was less so when a higher temperature of production was used. Conversely in the case of the MIX, phosphodiesterase activity increased as temperature increased. Phosphodiesterase is known for being involved in the breakdown of nucleic acids and phospholipids which are a chief component in fresh organic P inputs. Previous studies (insert ref.) have attributed increases in phosphodiesterase activity to increases in pH, though this is not in support of the results observed here, as the paunch hydrochars have lower pH than the soil. Whilst the MIX and DAF hydrochars have a pH closer to neutral, any liming effect would be considered negligible.

The effect of the amendments on β-glucosidase activity in the soil was minimal, in fact only the PAUNCH180 treatment changed β-glucosidase activity (1.1 times more than the control). The results indicate that the hydrochars had the same effect as the compost on enzymes which catalyze hydrolysis of complex carbohydrates, providing energy for microorganisms.

6.3. Calorific value of hydrochar

The higher heating value (HHV) of the six hydrochars is presented in table 6 below. The calorific values ranged from 21.4 MJ/kg (DAF180) to 27.2 (PAUNCH180). For both the paunch and a mix of paunch and DAF sludge hydrochars, the calorific value decreased as the temperature of production increased. In both cases 0.3 MJ/kg was lost as a result of the increase in temperature.
The author should include a full interpretation of the results.

7.0 CONCLUSIONS/RECOMMENDATIONS

The results of this preliminary study indicate that the conversion of abattoir waste to hydrochar is a promising alternative to composting. Three different waste streams were converted to hydrochar, under two production temperatures. In all cases the mass and volume of the waste stream was significantly reduced. In terms of fertilizer value, hydrochars produced from paunch and a mixture of paunch and DAF sludge led to a significant increase in wheat yield compared to the compost. On the other hand, the DAF sludge had no effect compared to the compost. In terms of value as a fuel, the hydrochars had a HHV comparable to lignite.

The study was limited by the use of a single soil which could be addressed in a future study involving several soil types or by way of a field trial. A more comprehensive, including the study of the kinetic parameters of hydrothermal carbonization, study would consolidate findings from this preliminary work and further guide the deployment of this technology in the Australian meat processing industry.

Overall our study has allowed to:

// Identify hydrothermal carbonization as an adequate technique to reduce the volumes of waste (up to 50 %). The elimination of prior drying compared to other techniques, such as pyrolysis, makes hydrothermal carbonization a more cost-effective technique.

// Identify the type of waste stream which should be utilized for hydrothermal carbonization (paunch waste or paunch waste mixed with DAF sludge and manure, but no DAF sludge alone).

// Conclude the potential to use the hydrochars obtained from paunch waste and a mix waste as soil conditioners in agriculture, even in a relatively fertile soil. In our study the addition of hydrochars resulted in a yield increase of up to 20 %, with respect to the use of compost and in an increase in soil enzymes (a proxy for soil quality).

// Our study has hinted the potential to produce hydrochars as solid clean fuels as a consequence of their intrinsic characteristics.

Uncertainty remains over which type of soils would be more suitable for hydrochar use and the optimal doses, which impedes to find the real market value of the product. It would be recommended to trial the product in different problem soils in order to establish the most suitable doses and conditions for hydrochar use.

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9.0 APPENDICES

Table 1: Hydrochar yield and HTC conditions

Sample	Yield (wt%)	Temperature (°C)	Time at final T (h)	Pressure achieved (bar)
PAUNCH-180-6h	56.2	180	6	7.5
PAUNCH-240-6h	49.5	240	6	19.4
MIX-180-6h	67.6	180	6	9.1
MIX-240-6h	59.5	240	6	17.9
DAF-180-6h	75.2	180	6	6.6
H-DAF-240-6h	75.2	240	6	12.4

Table 2: Hydrochar characterisation

Sample	H-PAUNCH-180-6h	H-PAUNCH-240-6h	H-MIX-180-6h	H-MIX-240-6h	H-DAF-180-6h	H-DAF-240-6h
VM (wt%)	69.68	52.67	45.28	41.24	96.15	95.15
FC (wt%)	28.04	44.53	12.78	15.54	0.72	0.69
Ash (wt%)	2.1	2.8	41.9	43.2	3.1	4.16
BET surface area (m^2/g)	8.5	12.9	6.7	7.4	-	-
Total pore area (m^2/g)	8.5	20.5	10.1	10	-	-
Porosity (%)	77.8	80	64.6	63	-	-
pH	5.26±0.07	5.22±0.01	6.81±0.15	6.78±0.01	6.31±0.02	6.36±0.10
EC (µS cm-1, 25°C)	26±2	40±2	49±2	53±1	13±2	10±2
CEC (cmol(+) kg-1	27.1±2.3	44.0±3.7	39.2±3.1	64.5±5.2	34.5±3.5	71.9±4.7
K2O (%)	1.4±0.1	2.1±0.2	1.7±0.1	2.9±0.1	1.0±0.1	1.7±0.1
P2O5 (%)	0.18±0.01	0.22±0.01	0.12±0.01	0.13±0.01	0.08±0.01	0.09±0.01
Cd (mg kg^{-1})	35±2	48±5	11±2	17±1	17±1	24±1
Cr (mg kg^{-1})	Below detection limit	Below detection limit	Below detec limit	Below detec limit	Below detec limit	Below detec limit
Cu (mg kg^{-1})	Below detection limit	Below detection limit	Below detec. limit	Below detec limit	Below detec limit	Below detec limit
Zn (mg kg^{-1})	552±20	652±48	576±4	783±23	528±21	616±10
Ni (mg kg^{-1})	36±4	52±5	165±8	196±31	49±3	50±5

Table 3: Soil characterisation

pH (1:2.5)	5.71±0.03
EC (1:2.5, µS cm-1, 25°C)	226±3
CEC (cmol(+) kg-1)	18.35±0.62
OC (%)	10.42±0.25
P_2O_5 (%)	0.1
K_2O (%)	0.1
Cd (mg kg-1)	6±1
Cr (mg kg^{-1})	27.2±4
Cu (mg kg^{-1})	13.8±1.2
Ni (mg kg^{-1})	34±2
Zn (mg kg^{-1})	51±5
Textural class (USDA)	Loamy sand
Sand (%)	74
Silt (%)	18
Clay (%)	8

Table 4: Wheat yield

Sample	(dry biomass in g)
Control-COMPOST	0.38±0.01a
H-PAUNCH-180-6h	0.46±0.01b
H-PAUNCH-240-6h	0.47±0.03b
H-MIX-180-6h	0.45±0.05b
H-MIX-240-6h	0.45±0.04b
H-DAF-180-6h	0.38±0.01a
H-DAF-240-6h	0.39±0.02a

Table 5: Enzymatic activity µmoles product g^{-1} h^{-1} of soil with different treatments after the 74-day incubation experiment.

Sample	Dehydrogenase	Phosphomonoesterase	β-glucosidase	Phosphodiesterase
Control-COMPOST	0.06±0.01a	3.38±0.18a	0.779±0.07a	0.22±0.03a
H-PAUNCH-180-6h	0.12 ± 0.02ab	3.24±0.26a	0.887±0.07b	0.34±0.05c
H-PAUNCH-240-6h	0.13 ± 0.05b	3.10±0.27a	0.848±0.02ab	0.29±0.01b
H-MIX-180-6h	0.09 ± 0.01ab	2.93±0.13a	0.832±0.04ab	0.42±0.02d
H-MIX-240-6h	0.20 ± 0.04c	1.28±0.06b	0.824±0.08ab	0.55±0.06e
H-DAF-180-6h	0.06±0.01a	3.08±0.08a	0.762±0.04a	0.25±0.01ab
H-DAF-240-6h	0.07±0.01ab	3.41±0.21a	0.820±0.03ab	0.27±0.01ab

The values in the columns with a common letter are not significantly different ($p > 0.05$) according to the Duncan test.

Table 6: Higher Heating Value of the hydrochars

Sample	HHV (MJ/kg)
H-PAUNCH-180-6h	27.2
H-PAUNCH-240-6h	26.9
H-MIX-180-6h	24.8
H-MIX-240-6h	24.5
H-DAF-180-6h	21.4
H-DAF-240-6h	21.5