HYDROTHERMAL CARBONISATION OF CATTLE PAUNCH WASTE

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DISCLAIMER

I hereby declare that this thesis is my own original work and further, I have acknowledged all sources used and have cited these in the reference section.
ABSTRACT

Meat processing and abattoir operations face several issues in regards with solid waste management worldwide. Presently, most wastes from slaughterhouses are landfilled, which not only causes major environmental damage, but also adds to running costs of the abattoir. In order to combat these issues, several waste treatment methods have been trialled, including conventional thermochemical processes such as pyrolysis and torrefaction. However, these methods were found to be economically unviable because the waste has to be dried prior to treatment. Hydrothermal carbonisation (HTC) overcomes this challenge and treats waste having moisture content of up to 90% at low temperatures, while generating value added products.

This project was focused on a particular abattoir waste known as paunch. Paunch waste is the undigested feed of cattle and makes up 10% of the animal’s weight. Different reaction temperatures (150, 180 and 200 °C) and times (1 and 4 h), as well as varied feedstock moisture contents (75 and 90%), were used in order to produce different grades of products. The fuel characteristics of the solid products were tested for potential use as energy source for electricity generation and the nutrient concentrations in the liquid products were analysed to verify their suitability as soil amendment.

The carbon content of the paunch waste improved by 10 to 15% after HTC and was also reflected on the calorific content of hydrochars, which increased by a maximum of 27%. The atomic H/C and O/C ratios decreased considerably from 1.760 and 0.633 to 0.451 and 0.234, respectively. The evolution of the H/C and O/C atomic ratios of the hydrochars were analysed using the van Krevelen diagram and it was found that the fuel properties of the hydrochars improved noticeably after carbonisation. The nutrient concentrations in the liquid phases were found to increase significantly with increasing reaction temperature and time. With increased moisture content, nutrient concentrations decreased, because of relatively higher water content. The liquid phase can therefore be used as fertiliser while the properties of the hydrochars suggest that they can achieve good performance as a fuel for electricity generation.
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<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>BOD</td>
<td>Biochemical oxygen demand</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
</tr>
<tr>
<td>FC</td>
<td>Fixed carbon</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform infrared spectroscopy</td>
</tr>
<tr>
<td>HHV</td>
<td>Higher heating value</td>
</tr>
<tr>
<td>HTC</td>
<td>Hydrothermal carbonisation</td>
</tr>
<tr>
<td>IC</td>
<td>Inorganic carbon</td>
</tr>
<tr>
<td>Mio. €</td>
<td>Million Euro</td>
</tr>
<tr>
<td>MW&lt;sub&gt;HHV&lt;/sub&gt;</td>
<td>Megawatt Power based on HHV</td>
</tr>
<tr>
<td>ND</td>
<td>Not determined</td>
</tr>
<tr>
<td>Rpm</td>
<td>Revolutions per minute</td>
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<tr>
<td>TC</td>
<td>Total carbon</td>
</tr>
<tr>
<td>TCI</td>
<td>Total capital investment</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>VM</td>
<td>Volatile matter</td>
</tr>
<tr>
<td>μS</td>
<td>Micro siemens</td>
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CHAPTER 1: INTRODUCTION

Coalification is a natural process which takes place under geological influences leading to the compression and heating of organic material over a long period of time (He, Giannis and Wang 2013). Hydrothermal carbonisation (HTC) is a thermochemical process used for the conversion of organic material to a charred matter which resembles the composition of coal but it is formed using much less time (Funke and Ziegler 2010). The fundamental scientific knowledge of HTC was compiled by Friederich Bergius in 1913 and has been further developed by the director of the Department of Colloid Chemistry at the Max-Planck Institute of Colloids and Interfaces, Professor Antonietti (Saetea and Tippayawong 2013). There has been a growing scientific interest in hydrothermal degradation of organic matter lately since its product could be a potential fuel in the future. This process has been developed in Europe but is not used in any Australian commercial or experimental plants at the moment (Mehta et al. 2014).

Hydrothermal carbonisation is achieved under aqueous conditions at temperatures ranging from 150 °C to 250 °C and high autogenous pressure to ensure that water remains in its liquid state (Shah 2014). The reaction occurs usually over several hours. There are three distinct phases produced; a solid phase known as the hydrochar as well as liquid and gas phases. Generally, in a weight basis, 50 to 80% of the original feedstock is present in the hydrochar, 5 to 20% is present in the liquid phase, and 2 to 5% is present in the gas phase (Libra, et al. 2011). Gas evolved during the process is minor and mainly consists of carbon dioxide (Wiedner, et al. 2013). The hydrochar is a high energy product that can be used as fuel for electricity generation and the nutrient-rich liquid phase can be used as a fertiliser.

1.1 Problem definition

Australia currently produces an approximate 2.6 million tonnes of meat annually and is the seventh largest beef producer worldwide (McCabe et al. 2016). This production results in a significant
amount of waste which not only is costly to dispose of, but also has negative impacts on the environment and farms throughout the country face this issue of waste disposal (McCabe et al. 2016). A large proportion of the waste produced is known as the paunch and it makes up approximately 10% of the total animal weight. During the processing of carcasses, cattle rumen, which is a part of the animal that is not consumable and therefore non profitable to any meat processing company, is removed (McCabe et al. 2016). The paunch is simply treated as waste, but before disposal it requires treatment which increases expenses in addition to transportation (McCabe et al. 2016). Paunch waste consists mostly of grass and grain, which has high carbon content and there can be about 40 kg of paunch waste per cattle (Mehta et al. 2014). Hydrothermal carbonisation (HTC) can be a potential solution for this issue and can turn this waste into useful products, while cutting down on the expenses associated with the treatment, transportation and disposal of the waste (Saetea and Tippayawong 2013).

Harvey Beef is a meat production company located 140 km south of Perth, Western Australia in the town of Harvey. The company slaughters around 140,000 cattle yearly (Harvey Beef 2017). This means that there are approximately 5600 tonnes of paunch waste from this particular slaughterhouse that are being disposed to landfill facilities on an annual basis. Harvey Beef was keen to find a sustainable way of disposing of the paunch waste. This project consists of developing an alternative method to paunch waste landfilling through hydrothermal carbonisation in subcritical water for the production of hydrochar and nutrient rich liquid fertiliser (Funke and Ziegler 2010). These products could then either be used by the facility or sold to other companies.

1.2 Objectives
The aim of this project is to develop a decentralized solution using hydrothermal carbonisation as an alternative for paunch waste disposal to landfills for Harvey Beef Pty Ltd. The influence of different operational parameters such as moisture content, reaction time and reaction temperature on the process will be investigated for process optimization. The main focus of this project is the
characterisation of the solid and liquid products, through different relevant analytical methods. Understanding the physical and chemical characteristics of the products is essential to test their various applications.

1.3 Outline
The introductory chapter is followed by chapter 2 which explores the theoretical background of hydrothermal carbonisation from its discovery to the recent years. HTC process conditions, process chemistry and analytic methods of biomass and products are discussed in this section. The methodology is covered in chapter 3 and explains in details all the materials used, procedure and underlying theory. This section also includes calculations, equipment, technique and analytical methods used. Limitations and assumptions involved in the experiments are also mentioned in this chapter. The results obtained from the experiments are presented in section 4, in the form of tables, graphs and succinct description of the observations made. Chapter 4 also includes the discussion part where all the results obtained are interpreted and compared to previous work. An energy balance is also included in this section. The conclusion and the recommendations are the two final sections of this report.
CHAPTER 2: LITERATURE REVIEW

Meat processing and abattoir operations face several issues in regards with solid waste management. These industries generate large amounts of paunch waste that has high levels of organics and nitrogenous compounds and is considered as a high biological risk solid waste as it contains various pathogens which represent a health risk to humans and animals (Steffen 2016). Improper storage of the waste can result in soil and water contamination and may cause public nuisance with respect to odour and attracting vermin. Atmospheric contamination result mostly from greenhouse gases emitted during treatment and transportation of the waste. Transporting paunch contents may also cause nutrient contamination to roads and waterways if spillage occurs (Steffen 2016).

In most abattoirs, the paunch contents are recovered from the effluent stream by screening after having been washed out of the rumen. Approximately 2 m$^3$ of dewatered paunch contents is produced for every 100 heads of cattle slaughtered. The dewatering step is essential for ensuing transportation and processing of the waste. At present, most meat processing industries around Australia are incinerating or disposing of the paunch waste to landfills (Ferreiro 2017). Statistics show that a large abattoir can produce more than 3000 tonnes of paunch waste annually and approximately 150 dollars are spent per tonne for its disposal (Ferreiro 2017).

There have been several methods developed to treat paunch waste at Australian abattoirs such as composting, vermin composting, anaerobic lagoons and ensilage but composting has been the most widely used technique. During composting, pathogens and environmental risks associated with paunch waste are reduced. Composted paunch has been proven to help loosen up extremely tight soil and provide beneficial effects for cropping. However, inappropriate management of the process may result in odour nuisance, health risks, leachate contamination and increased pests (Environmental Protection Authority 2017). Moreover, in order to be in accordance with agricultural regulations, insecticides have to be sprayed on the fields to eliminate pests attracted from odour (Franke 2009). Although composting has
been recommended as the best method to treat this waste, this practice costs more than the actual raw material and ends up not benefiting the meat processing company economically. It is therefore necessary to explore other treatment options (Ferreiro 2017).

In other parts of the world, wastes to energy technologies have been used to convert paunch waste to energy. Using the waste in this manner has helped reduce cost associated with its disposal. The decrease in cost is accomplished by reducing the weight and volume of the waste, energy recovery and toxic gas emissions in comparison to fossil fuels. However, comparatively lower energy tariffs in Australia have prevented a wider exploration of these options. These techniques could potentially be adopted if energy production is coupled with the production of useful by-products. Technologies such as fast and slow pyrolysis as well as torrefaction have been used to treat paunch waste. Pyrolysis is a thermochemical technique that has been explored and offers several advantages including zero emission of greenhouse gases, elimination of foul odours and reduction of residues (Ferreiro 2017). Torrefaction is considered as a milder form of pyrolysis. However, these methods are not the most favourable for the treatment of wet biomass such as paunch. The feed for pyrolytic processes are required to be practically dry which implies added costs and makes the process uneconomical. The feed for torrefaction can have a maximum moisture content of 15%. However, paunch waste can have up to 85% moisture, so it will have to be dried to allow the process to occur which renders it unprofitable (Environmental Protection Authority 2017).

Hydrothermal carbonisation however, is ideal for wet bio-waste and allows feedstock to have up to 90% moisture content. HTC therefore requires less energy input to treat wet solid waste compared to other pyrolytic technologies and also generates more solid product. HTC could also be more advantageous for meat process industry compared to common pyrolysis in terms of energy gains (Ferreiro 2017). Moreover, given the process conditions, it can be ensured that HTC products are completely sterilised with respect to any possible pathogens (Shah 2014).
2.1 Hydrothermal carbonisation

Hydrothermal carbonisation is usually carried out at temperatures ranging from 150°C to 250°C. In order to ensure that water remains in a liquid state and under an inert atmosphere, the pressure has to be slightly higher than the water saturation pressure (Mau, et al. 2016). Normally at temperatures between 200°C and 280°C, water has both acidic and basic behaviour because its ion dissociation constant is maximised (Mau, et al. 2016). It is also important to note that at these temperatures, water’s dielectric constant decreases and it acts more like a non-polar solvent. The behavioural change of water in relation to temperature is shown in Figure 2.1.

![Figure 2.1: Change in properties of water with temperature (Mau, et al. 2016)](image)

These changes cause a decrease in the feedstock’s O and H content through dehydration and decarboxylation reactions which in turn increase the C content and consequently increase the calorific value of the product (Funke and Ziegler 2010).

Several types of wet biomasses have been experimented for HTC in the past, including poultry manure, human waste, wood chips and grass. HTC of poultry litter was investigated at 200°C, 225°C
and 250 °C for 1, 2 and 3 h with moisture contents of 85, 90 and 95%, paying particular attention to the elemental composition and metal content of the hydrochar and the aqueous phase (Heilmann et al. 2014). HTC of lawn grass was carried out at 200 °C and 240 °C for 30 to 180 min to determine the chemical, energetic, and structural characteristics of HTC solid residues (Guo, et al. 2015). HTC of microalgae was carried at 250 °C for 1 h with moisture content 90% and found the composition of the hydrochar and the aqueous phase (Ekpo, et al. 2016). Rice husk was hydrothermally treated at temperatures ranging from 200 to 300 °C and reaction times varying from 2 to 12 h focusing on physiochemical properties of the hydrochars (Kalderis, et al. 2014).

2.2 Analytical methods

2.2.1 Wet biomass
After collection of the wet biomass, the moisture content is found by weighing the initial mass then drying it in the oven at around 105 °C for 24 h before re-weighing the dried sample. Proximate analysis of the feedstock is performed, most often using thermogravimetric analysis (TGA), to determine moisture, ash and volatile matter content. The fixed carbon percentage is determined by difference as shown in equation 2.1.

Fixed carbon (%) = 100 – ash (%) – volatile matter (%) – moisture content (%)                     (2.1)

The fuel ratio which is one of the factors that is necessary to rank the quality of a fuel, by indicating its ease of ignition and burnout, is calculated from equation 2.2 (He, Giannis and Wang 2013).

\[
\text{Fuel ratio} = \frac{\% \text{Fixed carbon}}{\% \text{Volatile matter}}
\]  

(2.2)

The higher heating value (HHV) of the sample is measured using a bomb calorimeter. HHV of a fuel, also known as gross calorific value, is the amount of heat released during the complete combustion of a specified amount of the fuel and is determined by bringing all the products of
combustion back to the original pre-combustion temperature and in particular condensing any vapour produced (Demirbaş 1997). Ultimate analysis can also be performed by determining the elemental composition of carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and oxygen (O) using an elemental analyser. The predicted HHV is generally calculated based on the unified HHV correlation for fuels, the elemental composition (C, H, N, S and O) and ash (A) % concentration by mass on a dry basis (Channiwala and Parikh 2002).

\[
\text{HHV (MJ/kg)} = 0.349C + 1.1783H + 0.1005S - 0.1034O - 0.0015N - 0.0211A
\]

(2.3)

The predicted HHV and the measured HHV can be compared to find the relative error and hence, the precision of the predicted method.

The functional groups of the untreated biomass are also analysed using the Fourier transform infrared (FTIR) spectroscopy. FTIR is a technique used to identify molecular components and structures in organic and some inorganic compounds (Mau, et al. 2016).

2.2.2 Hydrochar
After HTC, reactors are placed in an ice bath in order to stop the reaction. The solid and aqueous phases are usually separated using vacuum filtration or centrifugation. The wet hydrochars are weighed, dried in the oven and reweighed to find the hydrochar yield. Proximate analyses of the hydrochars are performed, most often using thermogravimetric analyser (TGA), to determine moisture, ash and volatile matter content (He, Giannis and Wang 2013). The fixed carbon percentage is determined by difference. The fuel ratio is calculated from equation 2.2.

The higher heating values (HHVs) of the samples are measured using a bomb calorimeter. Ultimate analyses can also be performed by determining the elemental composition of carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and oxygen (O) using an elemental analyser. The predicted HHVs are then calculated from equation 2.3. The measured HHV of the untreated biomass and hydrochars are compared to obtain the energy densification of the hydrochars.
which will help assess the calorific value improvement of the paunch waste at different process conditions (He, Giannis and Wang 2013).

\[
\text{Energy densification} = \frac{\text{HHV of dry hydrochar}}{\text{HHV of dry paunch waste}}
\] (2.4)

HTC is then quantified by the energy yield which is the product of energy densification and hydrochar yield (Mau, et al. 2016).

\[
\text{Energy yield (\%)} = \text{energy densification} \times \text{hydrochar yield}
\] (2.5)

The functional groups of the hydrochars are also analysed using FTIR (Reza, Mumme and Ebert 2015).

2.2.3 Aqueous phase
The aqueous phase is considered to be a nutrient rich phase which can be used as a fertiliser. The aqueous phases are usually tested for total (TC) and inorganic carbon (IC) using a TOC analyser. The total extractable total organic carbon (TOC) concentrations are expressed as the difference between TC and IC concentrations (Ekpo, et al. 2016). Two important features when dealing with fertilisers are the actual amount and the ratio of nutrients which is a relative amount of each nutrient. NPK ratios of 2:1:1 and 4:2:1 are generally considered ideal for macro-level monitoring of consumption of plant nutrients (Prasad 2009). In order to determine the NPK ratio, total nitrogen (N), phosphorus (P) and potassium (K) have to be analysed in the samples. The total phosphorus and reactive phosphorus concentrations present in the aqueous phases are most often measured by colorimetry using the ascorbic acid method (Ekpo, et al. 2016). The total nitrogen is determined by the Kjedahl method which involves acid digestion of an aliquot sample with concentrated sulphuric acid (H\textsubscript{2}SO\textsubscript{4}) together with the Kjedahl catalyst. Sample distillation into boric acid solution is followed by titration with concentrated H\textsubscript{2}SO\textsubscript{4} to measure the released ammonia (Ekpo, et al. 2016). The most common method for determining potassium
concentration in liquids involves the technique of emission flame photometry. This is based on the theory that an alkali metal salt drawn into a non-luminous flame ionises, gains energy from the flame and subsequently emits light of a typical wavelength. The intensity of the emission is proportional to the concentration of the element in the sample. A photocell detects the light emitted which is then converted into a voltage (Proehl and Nelson 1950).

Electrical conductivity (EC) and pH tests are also important as soils require a particular salinity and pH for proper plant growth. An electrical conductivity meter and a pH meter can be used to measure EC and pH respectively (Mau, et al. 2016).

2.3 Process conditions
The yield and quality of the products depends highly on the process conditions (Funke and Ziegler 2010). Hydrothermal carbonisation is principally governed by process conditions such as reaction temperature, reaction time and moisture content. It is important to understand the effect of different process conditions on the characteristics of HTC products in order to verify their various applications (Mau, et al. 2016).

2.3.1 Reaction temperature
Throughout the years of research and experimentation, temperature has been found to be the most influencing parameter of the process (Funke and Ziegler 2010). The yield of the solid HTC product has been found to decrease significantly with an increase in reaction temperature (Reza, Mumme and Ebert 2015). A 50% decrease in solid mass yield was observed after 30 minutes of HTC of lawn grass at 200 °C. A 62% decrease of the solid yield was observed at 240 °C for the same amount of reaction time. These reductions are attributed to the fact that the hemicellulose, lignin and cellulose in the raw biomass were hydrolysed and solubilised into water or partitioned to the aqueous phases (Guo, et al. 2015). Figure 2.2 illustrates the solid yield change with temperature for the hydrothermal carbonisation of poultry litter (Mau, et al. 2016). The diagram
shows that the hydrochar yield decreased with increasing temperature similarly to the other studies carried.

Figure 2.2: Influence of reaction temperature on hydrochar yield (Mau, et al. 2016).

HTC of microalgae revealed a hydrochar yield decrease of 0.5% from 190 to 210 °C (Heilmann, et al. 2010). HTC of rice husk also demonstrated a decrease in hydrochar yield of 12% from 200 °C to 300 °C. This decrease is related to the deoxygenating reactions such as dehydration and decarboxylation and volatile matter conversion, as the oxygen and hydrogen contents decrease with increasing temperature (Kalderis, et al. 2014). This trend was also observed with HTC of wheat straw digestate and as the product yield decreases, an increase in the ash content was observed. In fact, more than 32 % ash was found in hydrochar treated at 260 °C for 6 h compared to 16% in the initial digestate (Reza, Mumme and Ebert 2015).
Several studies show a general increase in the carbon content of the hydrochars with increasing temperature. HTC of lawn grass showed an augmentation of the carbon content of 3.25 and 7.73% from the original biomass to the hydrochar obtained at 200 °C and 300 °C respectively (Guo, et al. 2015). Hydrothermally treated rice husk also showed an increase of the carbon content from 36.1% in the initial biomass to 43 and 47% in the hydrochars obtained at 200 and 300 °C correspondingly (Kalderis et al. 2014). Elemental carbon content of wheat straw digestate hydrochars was observed to increase by 8.5% and 22.2% when increasing reaction temperatures from 180 to 240 °C (Reza, Mumme and Ebert 2015).

Determination of elemental composition of the material and the hydrochars is essential to investigate the degree of carbonisation. C, H and O fractions have been found to decrease considerably in absolute mass after hydrothermal treatment as opposed to the relative mass fraction. After HTC of lawn grass, C, H and O fractions decreased to 53.85%, 43.4% and 46.5% at 200 °C and to 44.89%, 29.07% and 33.27% at 240 °C respectively. This suggests that almost or over half of the elemental mass in the dried raw material was lost, mostly due to the solubilisation to aqueous phases. The most significant decrease occurred with the H and O fractions at 240 °C compared to 200 °C. This shows that dehydration and decarboxylation reactions were highly influenced by an augmentation of the reaction temperature (Guo, et al. 2015).

Atomic ratios of H:C and O:C are found from the elemental analyses and are used to plot a van Krevelen diagram which is necessary to examine the intensity of the carbonisation process and evaluate the energy quality of the hydrochars (Reza, Mumme and Ebert 2015). It is also a practical way to illustrate the effects of the process operational parameters on the hydrochar. The atomic ratio moves from upper right to lower left as the carbonisation progresses. A van Krevelen diagram for the HTC of poultry at different reaction times and temperatures (Mau, et
al. 2016) is presented in Figure 2.3 and the direction of the vector indicates the contribution of dehydration and decarboxylation.

![Van Krevelen diagram](image)

**Figure 2.3**: van Krevelen for poultry litter and the hydrochars in comparison with the four typical coals; peat, lignite, bituminous coal and anthracite (Mau, et al. 2016)

HTC of rice husk also revealed that the H:C and O:C ratios decreased with temperature rise. With the help of the van Krevelen diagram (Figure 2.4), it could be observed that the dehydration path was predominant at a higher temperature. The van Krevelen diagram also suggests an enhancement in the fuel properties at higher reaction temperatures. This is confirmed by the predicted HHVs, which indicate an 11.8% increase as the temperature is elevated from 200 °C (H-200-6) to 300 °C (H-300-6) (Kalderis, et al. 2014).
Studies from HTC of lawn grass also agreed on the same trend and found that there was an increase of HHV with increasing temperature. The HHV of the untreated biomass increased from 17 to 17.4 MJ/kg and 18.24 MJ/kg for the biomass treated at 200 °C and 240 °C respectively (Guo, et al. 2015).

### 2.3.2 Reaction time

Although temperature was found to be the most impactful parameter, reaction time remains an important condition which controls the process. HTC of lawn grass revealed that the hydrochar yield decreased from 50 to 46% when reaction time was increased from 30 to 180 minutes. However at 240 °C, the solid yield decreased from 38 to 31% with the same residence time increase. The yield of the product was lower at higher temperature because HTC of lignocellulosic biomass was a relatively slow process and the reaction rate was mainly governed by temperature (Guo, et al. 2015). The same trend was observed with HTC of rice husk as shown in Figure 2.4.
The carbon content was found to increase with reaction time. HTC of lawn grass showed that carbon content increased from 42.9 to 46.15% after 30 minutes at 200 °C treatment and increased further to 49.1% after 180 minutes at the same temperature (Guo, et al. 2015). HTC of rice husk demonstrated a similar trend highlighting a 27.96% decrease in volatile matter and a 17.14% increase in fixed carbon content when reaction temperature increases from 200 to 300°C, indicating condensation and polymerisation reactions at higher temperatures. Longer reaction time also had a similar but smaller effect on the carbon content (Kalderis, et al. 2014).

O and H fractions were found to decrease with increasing reaction time. For HTC of lawn grass, the O and H fractions decreased to 36% and 37.8% at 200 °C and to 23.59% and 23.07% at 240°C respectively. However, the carbon fraction at both temperatures showed less considerable change with prolonged reaction time. This indicates that the increase in the carbon content with increasing reaction time at each temperature resulted from the mass losses of O and H.
Hemicellulose and cellulose degradations as well as deposition of dissolved compounds are other justifications for the increase in carbon content (Guo, et al. 2015).

HHV of hydrochars obtained from HTC of lawn grass increased to 19.3 MJ/kg after 180 min of treatment at 200 °C and 20.54 MJ/kg at 240 °C for the same time. The change was attributed to the removal of low HHV components such as fragrance, oils and hemicellulose at 200 °C and degradation and conversion of cellulose at 240 °C (Funke and Ziegler 2010). H:C and O:C ratios were between 1.17 to 1.64 and decreased to 0.45 to 0.65 at 200 and 240 °C, respectively. This indicated that dehydration and decarboxylation occurred during the HTC process as residence time and temperature were increasing (Guo, et al. 2015). HTC of rice husk demonstrated an increasing trend at 300 °C, suggesting that a more complete carbonisation of the product can be achieved with longer residence times (Kalderis, et al. 2014).

2.3.3 Moisture content
Although changes in moisture content do not impact heavily on the process, it has been agreed that water is the best pathway for biomass carbonisation compared to other substrates such as oil (Funke and Ziegler 2010). There are no standard experimental set up for HTC but most research work has been carried out with moisture content of 85% or higher with only a few at values around 75% (Li, et al. 2013). However, most of those studies have not investigated in depth the effect of water content on the process outcomes. Research carried out has concluded that moisture contents of 75 and 85% did not affect hydrochar formation as there were no impacts on the hydrochar yield but higher energy outputs were achieved at higher moisture contents (Mau, et al. 2016). However it was not a significant increase. On the other hand, HTC experiments performed with 75 to 95% moisture content revealed that this process parameter might have some effects on the yield of the hydrochar. HTC of biomass conducted with 75 to 95% moisture content found that a decrease in moisture content decreased the hydrochar yield (Roman, et al. 2012). Studies suggest that higher water content favours the hydrolysis reactions which explains
lower solid yield (Basso, et al. 2013). Moreover, previous HTC experiments performed with moisture contents of 50 to 80% showed that the variations had no influence on the reaction kinetics (Funke and Ziegler 2010).

2.4 Characteristics

2.4.1 Paunch waste
Age and weight of the animal as well as the type of feed and the fasting time before slaughtering are all factors that determine the amount and kind of the paunch waste contents (Steffen 2016). The waste characteristics do not vary as extensively as expected from the industry’s broad array of process and waste conservation operations (Steffen 2016). Typical characteristics of the paunch contents collected from abattoirs include:

- **Biodegradability**
  Paunch mainly consists of grass and grains which are made up of mostly organic compounds. The waste generally has a high BOD content which makes suitable for biological treatment such as composting to generate stable and useful products.

- **Moisture**
  The paunch is separated from the cattle intestine after slaughtering and diluted to form a waste stream with 2-5% solid content and therefore tend to have moisture contents greater than 85%. This makes the paunch waste susceptible to microbial activity and odour production. Usually the waste is dewatered before being transported to landfills.

- **Nutrients**
  Paunch waste usually contains a valuable amount of nutrients including carbon (~12.6%) and nitrogen (~3.5 mg/g).
• **Pathogens**

Paunch waste contains high levels of microorganisms, including pathogens mainly due to high moisture levels and decomposition. Generally, paunch contains negligible amounts of toxic compounds and heavy metals.

• **pH**

The pH of the waste is neutral at around 7.0 (Environmental Protection Authority 2017)

### 2.4.2 Hydrochar

It was found that the largest components of hydrochars are alkyls followed by aromatics (Berge, et al. 2011). Literature also shows that hydrochars have more functional groups than bituminous coal, which is a grade of coal used for electricity generation, but with less carboxyl and hydroxyl groups. Research conducted on HTC of poultry litter showed that nearly 80% of the C present in the original biomass was retained in the hydrochar (Ramke, et al. 2009). Hydrochars have lower H:C and O:C ratios compared to the initial biomass (Basso, et al. 2013). Results from different experiments revealed that the calorific value of the hydrochar with respect to the initial biomass is enhanced by 1.4 to 1.6 times, which confirms potential energy exploitation of this product (Lu, Jordan and Berge 2012). The hydrochar has reduced equilibrium moisture content when compared to the original feedstock and consequently is less likely to deteriorate in storage (Funke and Ziegler 2010). Energy densification is the calorific value of the hydrochar in comparison to the calorific value of the initial biomass and studies show that it increases considerably with temperature and time. The reported range of energy densification is from 1.1 to 1.6 (Oliveira, Blöhse and Ramke 2013). Several studies demonstrated through mass balance analysis that most of the initial C and N were held in the hydrochar, at greater than 70% each.

### 2.4.3 Aqueous phase

Literature shows that the liquid phase has a high load of organics and inorganics (Funke and Ziegler 2010). It contains several organic compounds, such as acetic acid, aldehydes and alkenes, and aromatics such as furanic and phenolic compounds, which have been detected
experimentally (Berge, et al. 2011). The extractable total organic carbon (TOC) present in the liquid phase is of polar and aromatic nature, and a major portion of the TOC is of higher molecular weight (Libra, et al. 2011). The biochemical oxygen demand (BOD) to the chemical oxygen demand (COD) ratio was found to be over 0.3 in the aqueous phase (Basso, et al. 2013). HTC of poultry litter showed that initially, the aqueous phases had a pH of 7.5 which decreased to 5.1-5.8 after carbonisation. Literature suggests that the decrease in pH was a result of the formation of organic acids and carbon dioxide from the carbonisation of cellulosic feedstock (Mau, et al. 2016). Previous study on HTC of poultry litter reported a DOC concentration of 8340 mg/L before HTC and ranged between 19000 to 25000 mg/L after HTC. DOC concentration tended to decrease with increasing temperature and reaction time. The results for the HTC of wood chips showed a similar trend (Hoekman et al. 2011). Literature suggests that the initial DOC increase followed by a decrease in concentration with rising temperature is due to the organic compounds produced at low temperatures which continue to react with increasing temperature and time (Hoekman et al. 2011). The total nitrogen (TN) concentration of poultry manure was initially 1403 mg/L. The concentration was found to increase to 2290 mg/L at 180 °C and decrease again to its initial level as the temperature and time increased. The concentrations of phosphorus (P) varied from 940 to 2250 mg/L and ranged from 5870 to 6330 mg/L for potassium (K) (Mau, et al. 2016). It was also found that the aqueous phase retained an approximate of 10 to 15% of carbon and nitrogen, respectively (Mau, et al. 2016).

### 2.5 Economics of HTC

There are currently no commercial industrial-scale HTC plants in operation (Busch, et al. 2014). The economic feasibility studies conducted so far are based on assumptions from software models obtained from lab-scale experiments. Nonetheless, comparison of HTC treatment with other common uses of upgraded biomass can give insight into the practicality and prospects of hydrochar as a fuel.
Table 2.1: Overview of data of modelled industrial-scale HTC plants reported in literature (Busch, et al. 2014)

<table>
<thead>
<tr>
<th>Plant Capacity [MW_{HHV}]</th>
<th>Feedstock</th>
<th>Total Capital Investment (TCI) [Mio. €]</th>
<th>Specific Cost of Hydrochar [€ GJ(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.85 Palm Oil Empty Fruit Bunches</td>
<td>9.01</td>
<td>9.67</td>
<td></td>
</tr>
<tr>
<td>28.65 Palm Oil Empty Fruit Bunches</td>
<td>16.47</td>
<td>7.94</td>
<td></td>
</tr>
<tr>
<td>11.15 Short Rotation Forestry Poplar Wood Chips</td>
<td>12.88</td>
<td>12.94</td>
<td></td>
</tr>
<tr>
<td>11.15 Biodegradable waste</td>
<td>13.91</td>
<td>9.81</td>
<td></td>
</tr>
<tr>
<td>11.15 Short Rotation Forestry Poplar Wood Chips</td>
<td>6.98</td>
<td>114.68</td>
<td></td>
</tr>
<tr>
<td>55.75 Short Rotation Forestry Poplar Wood Chips</td>
<td>20.72</td>
<td>11.1</td>
<td></td>
</tr>
<tr>
<td>11.15 Wheat Straw</td>
<td>ND</td>
<td>13.3</td>
<td></td>
</tr>
<tr>
<td>55.75 Wheat Straw</td>
<td>ND</td>
<td>9.84</td>
<td></td>
</tr>
</tbody>
</table>

HTC is a process that requires wet biomass and high pressure and therefore an appropriate reactor is necessary to withstand the pressure. Literature suggests that such a reactor represents 8.5 to 21.3% of the total capital investment (TCI) depending on the plant capacity and feedstock used (Stermann, Erlach and Ziegler 2013). Generally, TCI depends on feed biomass and when a biomass containing residues is used, initial screening is necessary and increases TCI. Higher water content in biomass also increases TCI due to higher waste water treatment costs and increased fuel consumption for heating. Table 2.1 shows that the overall costs of the hydrochar production decreases when the plant capacity increases due to economies-of-scale effects. Smaller plants have higher labour costs and higher specific capital costs (Busch, et al. 2014). The type of feedstock used is also an essential element, for instance, poplar wood chips from short rotation forestry can make up for nearly two thirds of the final product price in large-scale facilities. Contrastingly, residual biomass such as sewage sludge, municipal organic waste and palm oil empty fruit bunches (EFB) produce supplementary income for the disposal of the waste material, hence decreasing the cost of hydrochar. However, coal was priced at 2.29 €/GJ in 2013 and clearly from the specific costs presented in Table 2.1, hydrochar cannot contend with bituminous coal so far. In order to compete with coal, actions such as reducing transportation costs, water recirculation for increased energy yield and decreased waste water treatment charges and higher CO\(_2\) avoidance costs can be taken (Busch, et al. 2014).
CHAPTER 3: METHODOLOGY

3.1 Materials
The biomass used for this project was cattle paunch. A site visit to Harvey Beef abattoir located 150 km to the south of Perth in Western Australia was organised to collect the paunch. During the visit at the slaughterhouse, the waste processing was investigated in order to understand the way the waste is dewatered and handled before disposal. 5 kg of paunch waste sample was collected in a bucket from the final waste stream and it was preserved in a cold room for use throughout the project.

Figure 3.1 (a): Washed paunch waste disposed in big containers before being transported to landfill

Figure 3.1 (b): Washed paunch waste

3.2 Experimental procedure
Firstly, a sample of the paunch waste was weighed and then oven dried for 48 h at 105 °C. The dried paunch was weighed again in order to calculate the moisture content of the biomass. The calculation of the moisture content is shown below using equation 3.1.

\[
\text{Moisture content (\%) } = \frac{(\text{Wet weight} - \text{dry weight})}{\text{Wet weight}} \times 100 \%
\]  

(3.1)
The operational parameters that were investigated were moisture content, reaction time and temperature. These three parameters were varied throughout the project to analyse how the different conditions affect the quality of the products. This will help find the optimum conditions for the process to produce the best results. Table 3.1 shows the process conditions under which hydrothermal carbonisation of paunch waste was performed.

**Table 3.1: Process conditions for HTC of paunch waste**

<table>
<thead>
<tr>
<th>HTC Temperature (°C)</th>
<th>HTC Time (h)</th>
<th>HTC Moisture content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>1</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>75</td>
</tr>
<tr>
<td>180</td>
<td>1</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>75</td>
</tr>
<tr>
<td>200</td>
<td>1</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>75</td>
</tr>
</tbody>
</table>

In order to obtain the desired moisture content in the biomass, the dry paunch had to be mixed with distilled water. The mass of water required was calculated as shown below in equation 3.2.

\[
\text{Mass of water (g)} = \frac{\text{Mass of dry paunch (g)} \times \text{desired moisture content (\%)} }{100 - \text{desired moisture content (\%)} } \tag{3.2}
\]

The volume of water to be added to the dry paunch was then calculated from equation 3.3 using the calculated mass of water and the density of water of 0.997 g/mL (Thermal Excel 2003).

\[
\text{Volume of water (mL)} = \frac{\text{Mass of water (g)}}{\text{Density of water (g/mL)}} \tag{3.3}
\]
The dry paunch was diluted with the appropriate volume of water and the sample was then transferred into a 200 mL Teflon lined reactor chamber enclosed in a stainless steel outer body. The reactor was tightened and secured properly before being placed in the oven at the desired temperature for the desired reaction time. Once the reaction time had elapsed, the sample was carefully taken out of the oven using heat protecting gloves, and placed under cold water for about 20 to 30 minutes to stop the reaction. Once the autoclave cooled down completely, it was loosened and opened cautiously and the sample was transferred to 60 mL vials. The hydrochars and the liquid phases were separated using a MSE Mistral 2000 centrifuge. The centrifuge was set at a rotational speed of 4000 rpm for 15 minutes to make sure the products were fully separate. After centrifugation, the hydrochars were transferred in pre-weighed oven dishes and placed in the oven to dry at 105 °C for 24 h. The hydrochars were re-weighed after the drying process to obtain the dry hydrochar weights which were used for the hydrochar yield calculations (equation 3.4). The liquid samples were stored at cold temperatures for analysis.

\[
\text{Hydrochar yield (\%) = } \frac{\text{Dry hydrochar weight}}{\text{Dry paunch weight}} \times 100 \% \tag{3.4}
\]

### 3.3 Analytical methods

#### 3.3.1 Proximate analysis of paunch and hydrochars

Proximate analyses of the paunch and the hydrochars were performed to determine moisture, ash, volatile matter, and fixed carbon contents. Thermogravimetric analysis was used to achieve these tasks. The analyses were carried out using a Perkin Elmer Simultaneous Thermal Analyser STA 8000. Step 1 was run under N₂ gas at a flow rate of 45 mL/min and a heating rate of 20 °C/min from the initial temperature to 150 °C to determine moisture content by weight difference. Step 2 was run under the same conditions to determine volatile matter content as weight loss from 150 °C to 600 °C. Moisture content and volatile matter experiments are performed under inert conditions to prevent the samples from oxidising. Subsequently, dry air
at the same flow rate was used to determine ash content as weight loss from 600 to 700 °C. The fixed carbon percentage was determined by difference. The fuel ratio was calculated from equation 2.2.

The HHVs of the samples were measured using a Gallenkamp Autobomb bomb calorimeter. Each sample was placed into a press to make a compact tablet and the mass, \( m_p \), of the pellet was measured. A firing wire was attached and firmly clamped between the 2 electrodes in the bomb cap. Approximately 10 cm of firing cotton was cut and twisted around the firing wire on one side while the other side was left hanging down and into the crucible. The firing cotton into the crucible was coiled and the tablet was placed into the crucible in such a way that it would sit on the end of the cotton. The crucible was swung into place. 1mL of distilled water was then pipetted into the bomb. The assembled cap was placed on the bomb and screwed tightly down the sealing sleeve. The bomb was then slowly filled with oxygen until a pressure of 20 bars was reached. The bomb was then placed into the calorimeter set up. The thermometer reader was used to read the initial temperature of the calorimeter. Afterwards, the ‘fire’ switch was depressed to ignite the tablet. Once the temperature stabilised, the final temperature reading was taken and the temperature change was calculated.

Temperature change, \( \Delta T (\degree C) = (T_f - T_i) \degree C \) \hspace{1cm} (3.5)

\[
HHV \ (J/g) = \frac{\text{effective heat capacity of apparatus } (1/C) \times \Delta T \ (\degree C)}{m_p \ (g)} \hspace{1cm} (3.6)
\]

\[
HHV \ (MJ/kg) = HHV \left( \frac{1}{g} \right) \left( \frac{1000 \ g}{kg} \right) \times \frac{1 \ MJ}{1000000 \ J} \hspace{1cm} (3.7)
\]

**3.3.2 Ultimate analysis of pach and hydrochars**

Ultimate analyses was performed by determining the elemental composition of carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) using a ThermoFisher Scientific Elemental
Analyser FLASH HT and the samples were weighed into tin cups on a 1 μg resolution electronic balance.

The measured HHV of the untreated biomass and hydrochars were compared to obtain the energy densification (equation 2.4) of the hydrochars which helped assess the calorific value improvement of the paunch waste at different process conditions. HTC was then quantified by the energy yield (equation 2.5) which is the product of energy densification and hydrochar yield.

The carbon recovered in the hydrochar was also calculated using the following equation.

\[
\text{Carbon recovery (\%)} = \frac{\text{Carbon content in hydrochar (\%)}}{\text{Carbon content in paunch (\%)}} \times \text{hydrochar yield (\%)}
\]

(3.8)

The atomic H/C and O/C ratios were calculated based on the elemental analysis.

\[
\text{H/C ratio} = \frac{\%H}{\text{atomic mass of H}} \div \frac{\%C}{\text{atomic mass of C}}
\]

(3.9)

\[
\text{O/C ratio} = \frac{\%O}{\text{atomic mass of O}} \div \frac{\%C}{\text{atomic mass of C}}
\]

(3.10)

These ratios were then used to plot a van Krevelen diagram which helped to depict the reaction pathways, including dehydration and decarboxylation.

3.3.3 Energy balance
Energy balance was performed for each HTC reaction by calculating the energy required for the HTC process and the energy produced by the hydrochar combustion. The energy required to heat and to maintain the reactor at the desired temperature was not included in the input energy calculation since these values depend on the reactor design and operational procedures. The wet biomass was taken to be a non-reactive mixture of water and dry solids and therefore the
energy necessary to heat the sludge was calculated as the addition of the energy required to heat the water and the dry biomass as according to equation 3.11.

\[ Q_{in} = m_w (H_{w,HTC} - H_{w,25}) + m_s C_p (T_{HTC} - 25) \] (3.11)

where \( Q_{in} \) is the energy input for the HTC process, \( m_w \) and \( m_s \) are the water and solid masses in the mixture, respectively, \( H_{w,HTC} \) and \( H_{w,25} \) are the enthalpy of water at the process temperature and at 25 °C, respectively, \( C_p \) is the specific heat capacity of the dry biomass, 1.63 kJ/kg °C (Ahn, et al. 2009), and \( T_{HTC} \) is the process temperature.

The energy output was calculated as shown in equation 3.12.

\[ Q_{out} = m_h \Delta H^*_c \] (3.12)

Where \( m_h \) is the hydrochar mass and \( \Delta H^*_c \) is the heat of combustion of the hydrochar expressed as HHV.

The ratio of \( Q_{in} \) to \( Q_{out} \) corresponds to the energy fraction produced from the hydrochar combustion that is required to fuel the process.

3.3.4 Fourier Transform Infrared (FTIR) spectroscopy

FTIR is a useful analysis tool for characterising and identifying organic molecules. The attenuated total reflectance (ATR) mode for an FTIR spectroscopy allows functional groups present over a depth of about 1 μm to be identified (Drioli, Giorno and Fontananova 2010). The hydrochars were analysed with the PerkinElmer Frontier FTIR/NIR Spectrometer and the PerkinElmer Universal ATR Sampling Accessory within an absorbance range of 4000 to 400 cm\(^{-1}\). The diamond crystal plate of the machine was cleaned with isopropanol before each sample was analysed to ensure that there were no residues of previous samples. A baseline was first run to make sure that there was no noise identified on the spectrum which normally would indicate that the diamond plate was not properly cleaned. The sample was then placed on the
diamond tip and pressed by tightening the pressure tower until the force gauge reached 100 N and a spectral image of the hydrochar was obtained. FTIR data processing was carried out after spectral acquisition using Spectrum spectroscopy software.

3.3.5 Aqueous phases

The TPS labCHEM pH and conductivity meter was used to measure pH and electrical conductivity of the aqueous samples.

The Marine and Freshwater Research Laboratory (MAFRL) at Murdoch University carried experiments for the determination of the total extractable organic carbon (TOC), total nitrogen (TN) and the potassium (K) concentrations in the aqueous samples.

3.5 Limitations and assumptions

There were a few limitations encountered during the project most of which could not be controlled. However, there were some assumptions taken to adjust to the limitations and fulfil the project requirements and objectives.

Although it was known that gases such as CO$_2$ and H$_2$S are produced during HTC, the calculations energy balance excluded the gas phase given that it normally makes up only a small percentage of the final product (He, Giannis and Wang 2013). When performing the energy balance of the process, the energy required to heat and to maintain the reactor at the desired temperature was not included in the input energy calculation since these values depend on the reactor design and operational procedures and it would require more information of the product.

Since there were no equipment available to measure sulphur (S) in the solid samples, it was omitted from the ultimate analysis given that the other elements were more prominent and sulphur was only a minor percentage.
CHAPTER 4: RESULTS AND DISCUSSION

4.1 Hydrochar characterisation

The physical traits of the hydrochars obtained from the HTC of paunch waste provided useful insight on the carbonisation progress (Figure 4.1). With increasing carbonisation temperature, the hydrochars tended to be darker in colour and ashier in texture. Increasing residence time had a similar effect; however, the carbonised appearance was more intensified with temperature. The more carbonised hydrochars had a nut-like smell. There was no visual change due to variations in moisture content.

![Increasing temperature and reaction time](image)

Figure 4.1: Hydrochars produced shows advanced carbonisation with increased temperature and time

4.1.1 Physiochemical properties

The hydrochar yield decreased with increasing reaction temperature and time. Temperature was a key factor after 150 °C which is when the most significant decrease in the solid yield occurred (Figure 4.2). Reaction time also had a major influence on the solid product yield. As the reaction time increased, the product yield decreased and the effect of time was enhanced with increasing temperature. Moisture content affected hydrochar yield very slightly. Hydrochar yield was similar for 75% and 90% moisture contents after 1hr of reaction; however, after a carbonisation period of 4hr, biomass with lower moisture contents yielded more products. This trend was also observed for the HTC of lawn grass which showed a 50% decrease in solid mass.
yield after 30 minutes at 200 °C and a 62% decrease of the solid yield at 240 °C for the same amount of reaction time (Guo, et al. 2015).

![Figure 4.2: Influence of operational parameters and process conditions on hydrochar yield](image)

Table 4.1 shows that the carbon (C) content of the biomass increased gradually with increasing carbonisation temperature and time. The calorific value of the hydrochars, represented as the HHV, is mainly dependent on their C content when their proportion is bigger than the H content (Channiwala and Parikh 2002). Given that the C content increased, it was expected that the calorific value of the biomass would also increase and there was in fact a considerable rise. The calorific values of hydrochars obtained at 150 °C did not differ much from the calorific value of the original biomass. However, as temperature and time increased, the calorific value increased significantly (Figure 4.3). Similarly to the C content, the calorific value was also not affected by moisture content. The hydrochar with the highest calorific value was obtained at the
highest temperature (200 °C), longest reaction time (4 h) and lowest moisture content (75%). The calorific value was enhanced by 27.4% and is within the range of bituminous coal which is commonly used for electricity generation.

Energy densification of the hydrochars improved considerably when compared to the untreated paunch waste. It varied from 1.03 to 1.27 which corresponds to literature values of complex feedstock (Mau, et al. 2016). The carbonisation process releases energy through exothermic reactions and therefore not all the energy stored in the original biomass is present in the hydrochars (Mau, et al. 2016). The process was quantified as energy yield which ranged from 69 to 98%, slightly higher than the values obtained from studies for other complex feedstock. The hydrochar obtained at 150 °C and 1 h resembled the untreated biomass because of the low carbonisation temperature and short reaction time. The carbonisation progress was very small which explains the high hydrochar yield.

Figure 4.3: Influence of operational parameters and process conditions on calorific value
The proximate analysis of the hydrochars is presented in Table 4.1. The volatile matter (VM) content of the hydrochars decreased with both increasing reaction temperature and time but more significantly with temperature. VM decreased by approximately 5% at temperatures above 180 °C but only by 2% at lower temperatures. The moisture content of the biomass did not affect the volatile matter content. The ash content increased with increasing temperature and time mainly due to the loss of volatile matter and the retention of minerals in hydrochars (He, Giannis and Wang 2013). Here again, temperature was the most impacting parameter and had a greater influence above 180 °C demonstrating nearly 2% increase compared to only 0.5% increase at lower temperatures which indicates that the carbonisation process is intensified above 180 °C. The fixed carbon (FC) was found to increase as temperature and time increased. The change is attributed to the devolatisation of VM and mass conversion during the process. FC contents were similar with varying moisture contents indicating that this particular parameter did not have a lot of influence on the process (He, Giannis and Wang 2013). The fuel ratio experienced a gradual increase from 0.011 to 0.133, with increasing temperature and time, due to the decrease in VM and increase in FC. This reveals that the fuel rank of hydrochars is considerably improved through increased carbonisation conditions.

The ultimate analyses (Table 4.1) of the hydrochars were conducted to obtain their elemental composition.
Table 4.1: Chemical characteristics and fuel properties of hydrochars

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Temperature (°C)</th>
<th>Proximate analysis</th>
<th>Ultimate analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (h)</td>
<td>Paunch waste</td>
<td></td>
</tr>
<tr>
<td></td>
<td>150</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>180</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Moisture content (%)</td>
<td>75</td>
<td>90</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>6.70</td>
<td>8.97</td>
<td>9.70</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>91.75</td>
<td>85.06</td>
<td>85.68</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>-</td>
<td>3.75</td>
<td>2.77</td>
</tr>
<tr>
<td>Fixed carbon (%)</td>
<td>1.05</td>
<td>2.22</td>
<td>1.85</td>
</tr>
<tr>
<td>Fuel ratio</td>
<td>0.011</td>
<td>0.026</td>
<td>0.022</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>23.58</td>
<td>25.16</td>
<td>24.54</td>
</tr>
<tr>
<td>Hydrochar yield (%)</td>
<td>-</td>
<td>92.50</td>
<td>88.73</td>
</tr>
<tr>
<td>Energy densification</td>
<td>-</td>
<td>1.07</td>
<td>1.04</td>
</tr>
<tr>
<td>Energy yield (%)</td>
<td>-</td>
<td>98.69</td>
<td>92.33</td>
</tr>
<tr>
<td>C (%)</td>
<td>46.4</td>
<td>58.3</td>
<td>56.7</td>
</tr>
<tr>
<td>H (%)</td>
<td>6.80</td>
<td>2.74</td>
<td>5.97</td>
</tr>
<tr>
<td>O (%)</td>
<td>39.15</td>
<td>23.59</td>
<td>22.92</td>
</tr>
<tr>
<td>N (%)</td>
<td>1.0</td>
<td>6.4</td>
<td>4.7</td>
</tr>
<tr>
<td>H/C</td>
<td>1.759</td>
<td>0.564</td>
<td>1.264</td>
</tr>
<tr>
<td>O/C</td>
<td>0.633</td>
<td>0.304</td>
<td>0.303</td>
</tr>
<tr>
<td>Carbon recovery (%)</td>
<td>116</td>
<td>108</td>
<td>109</td>
</tr>
</tbody>
</table>
The carbon (C) contents of the hydrochars were observed to increase with both increasing carbonisation temperature and time. The C content initially increased from 46.3% in the paunch waste to 58.3% after 1 h treatment at 150 °C and continued to rise slightly and gradually from 58.3% to 60.7% after 1 h and 4 h carbonisation process at the same temperature, respectively. It was also noted that the C content of the hydrochar treated at the highest temperature for 1 h was lower than the C content of the hydrochar treated at the lowest temperature for 4 h. This indicates that reaction time influenced the C proportion of the solid product the most, mainly because the process temperatures used were lower than the average temperatures used in previous works. The moisture content however, was a neutral parameter since it did not have a prominent effect on the C content. High carbon recoveries (Table 4.1) ranging from 79 to 116% were obtained. This indicates that most of the carbon remained in the solid phase, which relates to a previous study carried out on HTC of rice husk, where carbon recoveries of 108 and 113%
were obtained (Kalderis, et al. 2014). The decrease of the carbon fraction in the solid phase with increasing temperature was attributed to the transfer of carbon to the liquid and gaseous phases through decarboxylation and other chemical reactions. The trend obtained agrees with previous studies that show that carbon recovery decreased with increasing temperature (Mau, et al. 2016).

O and H contents were found to both decrease significantly with increasing reaction temperature and time. Once more, it was found that moisture content did not influence the other elements of the process significantly. The O content of hydrochars decreased significantly from 39.14% to 19.79% as a result of dehydration and decarboxylation reactions. The H content was reduced by a maximum of 5.32% from the original biomass. Previous studies on HTC of rice husk and wheat straw also show similar trends (Kalderis, et al. 2014, Reza, Mumme and Ebert 2015). Literature attributes the increase in carbon content to the degradation of hemicellulose and cellulose as well as deposition of dissolved compounds (Guo, et al. 2015). In this experiment, at 200 °C, the O and H contents increased slightly because the increase in the C content at this temperature was smaller than at 150 °C and 180 °C. This could have been caused by slowing down of the degradation of materials.

The atomic H/C and O/C ratios reduced from 1.76 and 0.633 to 0.451 and 0.234, respectively. The evolution of the H/C and O/C atomic ratios of the hydrochars were analysed using the van Krevelen diagram in Figure 4.5. Following the reaction pathway of the paunch to the hydrochars, it can be observed that dehydration is predominant, as it was found in previous studies, while decarboxylation is hardly present similarly to the research conducted on HTC of microalgae (Heilmann, et al. 2010). Many studies suggest that temperature was the most influential parameter for more intense carbonisation. However, in this particular experiment, it
was found that both temperature and time have almost equal impact on the carbonisation progress mainly because in earlier research carried, temperatures above 200 °C were used.

**Figure 4.5: van Krevelen diagram showing the position of the hydrochars produced from paunch waste with 75% moisture content among known fuels**

For comparison, three typical fuels including, lignite, bituminous coal and anthracite were also plotted in the van Krevelen diagram (He, Giannis and Wang 2013). The illustration shows an improvement in the fuel properties of the hydrochars as they move closer to the bituminous coal region when temperature and time increases. This is confirmed by the HHVs of the hydrochars which reached a maximum of 30.04 MJ/kg, comparable to the calorific value of coal. Literature suggests that co-combustion of blended hydrochars and coal can achieve good performance for electricity generation (He, Giannis and Wang 2013).
4.1.2 Fourier Transform Infrared (FTIR) spectroscopy analysis

Figure 4.6: FTIR spectrum of dry paunch waste

The FTIR spectra were assigned into six regions which represent the main identification peaks.

It seemed that there were no considerable changes in FITR spectra of hydrochars.

(i) The peak at 3280 cm⁻¹ represents the –OH stretching vibration in the hydroxyl or carboxyl groups, indicating the presence of free and intermolecular-bonded groups. The relative intensity of the peak decreased slightly with rising temperature. It is probably related to the dehydration of the paunch material that normally occurs during HTC as it can be observed in the van Krevelen diagram (Chemistry Libre Texts 2014).

(ii) The bands centered around 2920 cm⁻¹ and 2850 cm⁻¹ were attributed to asymmetric and symmetric –CH stretching of the methylene groups respectively. The peaks of the hydrochars became relatively more intense as temperature and reaction time increase when compared with the initial feedstock’s peak (Chemistry Libre Texts 2014).

(iii) The peak at 1740 cm⁻¹ was assigned to the C=O stretching in the aldehyde group which slightly decreased in the hydrochars with increasing temperature and time. This could be an indication of decarboxylation reaction (He, Giannis and Wang 2013).

(iv) The peak at 1460 cm⁻¹ is associated with C=C stretching in aromatic ring carbons which is probably due to the lignin groups. The peaks increased slightly with increasing
temperature, demonstrating that as other components in the feedstock degraded, more lignin was present (Mau, et al. 2016).

(v) The increase in the relative intensity of the peak at 1030 cm$^{-1}$ was attributed to stretching of –COR in aliphatic ethers and –COH in alcohols. However, this peak also corresponds to –SiO stretching usually due to the presence of SiO$_2$ (Mau, et al. 2016).

(vi) The peak 720 cm$^{-1}$ was attributed to aromatic –CH out-of-plane bending vibrations in aromatic nucleus –CH structure. The slight increase of this peak with increasing temperature and time indicates that high carbon aromatization occurred during HTC. These results coincides with literature findings (He, Giannis and Wang 2013)

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**Figure 4.7: FTIR spectrum of hydrochar after 1 h at 150 °C**

**Figure 4.8: FTIR spectrum of hydrochar after 4 h at 150 °C**
Figure 4.9: FTIR spectrum of hydrochar after 1 h at 180 °C

Figure 4.10: FTIR spectrum of hydrochar after 4 h at 180 °C

Figure 4.11: FTIR spectrum of hydrochar after 1 h at 200 °C
4.2 Aqueous phase characterisation

Similarly to the hydrochars, the liquid phase also darkened in colour with increasing carbonisation time and temperature. The liquid had an oil layer which was potentially transferred from the paunch waste known to have considerable grease content from animal fat.

4.2.1 Electrical conductivity and pH

The electrical conductivities (EC) and pH are presented in Table 4.2. The pH of the aqueous phases ranged from 4.8 to 5.6 and decreased with increasing temperature and time mainly due to the formation of organic acids and carbon dioxide from the carbonisation of cellulosic feedstock (Mau, et al. 2016). The moisture content in the initial biomass did not affect the pH of the final liquid product to a large extent. The electrical conductivities varied from 590 – 10800 μS and increased with increasing temperature and time. Aqueous phases derived from biomasses with lower moisture contents (75%) had electrical conductivities that were significantly larger (~ 37%) than those derived from biomasses with higher moisture contents, potentially due to the more concentrated level of ions in aqueous phases of lower moisture contents.
Table 4.2: Aqueous phase characteristics

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<th>200</th>
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<td></td>
<td>Time (h)</td>
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<td>1</td>
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<tr>
<td>Moisture content (%)</td>
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<td>90</td>
<td>75</td>
<td>90</td>
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<tr>
<td>TOC (mg/L)</td>
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<td>2800</td>
<td>1500</td>
<td>22000</td>
</tr>
<tr>
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4.2.2 Nutrients

The total organic carbon (TOC) ranged from 2800 to 35000 mg/L. Increasing temperature and reaction time showed an increase in TOC concentrations by a factor of approximately 10. Previous works show that the TOC increased initially but decreased after 200 °C. However, in this experiment the maximum temperature used was 200 °C. It was suggested that the initial increase is mostly due to the organic compounds formed at low temperatures and these organic compounds could be acetic acid, aldehydes, alkenes, furanic and phenolic compounds, commonly present in the liquid product (Mau, et al. 2016). The decrease in the carbon recoveries of the hydrochars with increasing temperature and time also demonstrate that a fraction of the total biomass carbon was transferred to the aqueous phase, hence the increase of TOC with increased temperature and time.

The total nitrogen (TN) ranged from 310 to 8600 mg/L. TN concentrations increased initially from 150 to 180 °C then declined at 200 °C which corresponded to the trend obtained in literature (Mau, et al. 2016). It is suggested that organic compounds formed at lower temperatures react at higher temperatures which explains the TN concentration decline after 180 °C.

Potassium (K) concentration ranged from 50 to 310 mg/L. It did not vary significantly with temperature and time. However, aqueous phases obtained from biomass of higher moisture contents showed considerably lower carbon and nutrient concentrations, most probably because of the larger volume of water in the initial feedstocks.
### 4.3 Energy balance

#### Table 4.3: Energy balance of HTC process

<table>
<thead>
<tr>
<th>HTC Temperature (°C)</th>
<th>HTC Time (h)</th>
<th>HTC Moisture content (%)</th>
<th>Energy to heat water (kJ)</th>
<th>Energy to heat paunch (kJ)</th>
<th>Input energy, Q&lt;sub&gt;in&lt;/sub&gt; (kJ)</th>
<th>Output energy, Q&lt;sub&gt;out&lt;/sub&gt; (kJ)</th>
<th>Fraction of hydrochar combustion energy required for energy input (%)</th>
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<tbody>
<tr>
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<td>75</td>
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<td>34.3</td>
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<td>90</td>
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<td>1.36</td>
<td>33.3</td>
<td>79.1</td>
<td>42.1</td>
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</table>

The total energy input was governed by the proportion of water in the paunch, which accounted for around 90-95% of the total required to heat the paunch. For this reason, the feedstocks with higher moisture contents required more input heat energy compared to feedstocks with lower moisture contents. Similarly, increasing reaction temperature and time caused an increase in the energy input since more energy was required to heat the solids in the feedstocks. Energy output was largely dependent on the hydrochar yields and their calorific values. Energy output was observed to decrease by 19-25% with rising temperatures, as demonstrated with the hydrochar yield trend. This indicates that the energy output was mostly affected by the hydrochar yield rather than the calorific value which was observed to increase with increasing temperature. Reaction time was also shown to cause a decrease in the energy output of the solid products and once again the hydrochar yield proved to be the more influencing value. However, despite the overall lower energy output at higher temperature and time, the energy per unit weight of hydrochar is significantly higher, ensuring a better quality hydrochar. The temperature and hydrochar quality should be taken into account since it is planned to use the product for energy production. Energy output is considerably larger at lower moisture
contents, since more organic matter is originally present per unit mass of the feedstock. Approximately 7-40% of the total hydrochar combustion energy would be necessary to provide the input energy required for the process. Although these fractions do not include the energy needed to heat and maintain the reactor at the desired HTC temperature, nor does it take into consideration for heat losses, optimised design and operational procedure can help keep these percentages to a minimum.
CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The aim of this thesis was to develop a decentralised solution using hydrothermal carbonisation as an alternative for paunch waste disposal to landfills for Harvey Beef Pty Ltd. HTC is a promising technology as it treats waste having up to 90% moisture content at low temperatures. HTC therefore requires less energy input to treat wet solid waste compared to other pyrolytic technologies which require prior drying. Given that moisture content of the initial paunch waste was 75%, hydrothermal carbonisation was an ideal solution. Paunch waste of varying moisture contents were treated in subcritical water at different reaction temperatures and times to obtain different grades of products. The influence of each process operational parameter on the products obtained was investigated by characterising the solid and liquid phases through several analytical methods.

Temperature and time had the most significant effect on the process and product formation. Moisture content of the biomass was not a major factor once dilution effects were considered. With increasing carbonisation temperature, the hydrochars tended to be darker in colour and ashier in texture. The more carbonised hydrochars had a nut-like smell. It was found that the fuel properties of paunch waste improved significantly after hydrothermal carbonisation. As a consequence of higher fixed carbon and lower volatile matter, hydrochars achieved a fuel ratio high up to 0.133 from the original biomass having fuel ratio of 0.011. Hydrothermal carbonization of paunch waste provided hydrochars with energy contents in the bituminous coal range. The carbon content of the paunch waste increased by up to 15% and since the calorific value of biomass is dependent on carbon content, it was expected that the calorific value would increase as well. In fact, the calorific value of the original biomass increased by up to 27% after HTC. Energy densification of the hydrochars improved considerably when compared to the untreated paunch waste. It varied from 1.03 to 1.27 which corresponds to literature values of complex feedstock. Although carbon recovery decreased with increasing reaction temperature and time due to carbon transfer in the liquid phase, 79% of
carbon was still retained in the solid product. The atomic H/C and O/C ratios decreased considerably from 1.760 and 0.633 to 0.451 and 0.234, respectively. These ratios were used to plot a van Krevelen diagram which showed that dehydration was the predominant reaction during the process. The aqueous phase was characterised as a nutrient dense and carbon rich product which suggests its use as a liquid fertiliser while the properties of the hydrochars imply that they can achieve good performance for electricity generation.

5.2 Recommendations
This thesis has focused on treating paunch waste collected from Harvey Beef abattoir using hydrothermal carbonisation and characterising the solid and liquid products obtained. However, further work has to be carried out to ensure that the company has a more sustainable future in terms of solid waste management.

- Carry out HTC of paunch waste at temperatures higher than 200 °C
  This experiment was carried out at temperatures of 200 °C and lower, but literature suggests that temperatures within 200 and 250 °C yield higher quality products in terms of calorific value, energy yield, and atomic H/C and O/C ratios (Kalderis, et al. 2014). Therefore, it is important to characterise of the paunch waste processed at higher temperatures.

- Test application of liquid fertiliser
  Although the aqueous phase has been analysed for chemical properties in this thesis, further experiments need to be carried out to observe how plants react to its use and test its suitability for use as a liquid fertiliser. Moreover, if required, experiments should be performed to improve its quality for that purpose.

- Combustion behaviour analysis
  The determination of kinetic parameters is essential to better understand the combustion behaviours of the hydrochars. The activation energy and pre-exponential factor are two
fundamental kinetic parameters that are necessary to assess the difficulty and intensity of combustion reactions for fuels (He, Giannis and Wang 2013).

- Process design, modelling, energy efficiency and cost analysis of HTC plant for Harvey Beef Pty Ltd

In terms of implementation, modeling and designing an appropriately sized HTC continuous plant for Harvey Beef paunch waste reuse is necessary. HTC process is to be designed and modelled on the basis of laboratory data of experimental runs from this project. Thermal and electric energy specific consumption as well as plant energy efficiencies should be analysed to achieve a more sustainable output. A financial evaluation of the investment, process and running costs should then be performed based on the plant design and model.

- Life-cycle assessment

A life cycle assessment is required to analyse the total environmental impact of the HTC design. The environmental assessment of HTC coal generation and usage is required using carbon footprinting, as part of the life-cycle assessment method, which is globally standardised in accordance with ISO 14040 and ISO 14044 (Zeymer, et al. 2017).
REFERENCES


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Wiedner, Katja, Cornelia Rumpel, Christoph Steiner, Alessandro Pozzi, Robert Maas, and Bruno Glaser. “Chemical evaluation of chars produced by thermochemical conversion (gasification, pyrolysis and hydrothermal carbonization) of agro-industrial biomass on a commercial scale.” *Biomass & Bioenergy* 59 (2013): 264-278.

**APPENDICES**

**Appendix 1: Higher Heating Value Calculation**

<table>
<thead>
<tr>
<th>HTC Temperature (°C)</th>
<th>HTC Time (h)</th>
<th>HTC Moisture content (%)</th>
<th>Mass of pellet, $m_p$ (g)</th>
<th>Initial temperature, $T_i$ (°C)</th>
<th>Final temperature, $T_f$ (°C)</th>
<th>Temperature change, $\Delta T$ (°C)</th>
<th>HHV (J/g)</th>
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Appendix 2: Energy Balance Calculation

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<th>HTC Temperature (°C)</th>
<th>HTC Time (h)</th>
<th>HTC Moisture content (%)</th>
<th>mass of water, ( m_w ) (kg)</th>
<th>mass of solid, ( m_s ) (kg)</th>
<th>mass of hydrochar, ( m_h ) (kg)</th>
<th>HHV (kJ/kg)</th>
<th>Energy to heat water (kJ)</th>
<th>Energy to heat hydrochar (kJ)</th>
<th>Input energy, ( Q_{in} ) (kJ)</th>
<th>Output energy, ( Q_{out} ) (kJ)</th>
<th>Fraction of hydrochar combustion energy required for energy input (%)</th>
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Appendix 3: Aqueous phase analysis by MAFRL

INTERIM REPORT
MARINE AND FRESHWATER RESEARCH LABORATORY
WATER QUALITY DATA

Contact: Gwenella Saverettiar
Customer: School of Engineering and IT, Murdoch University
Address: 90 South Street, Murdoch, WA 6150

Date of Issue: 23/05/2018
Date Received: 10/05/2018
Our Reference: ENG18-2

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Note: Only aqueous phase analysed