Evaluation of suitability of water hyacinth as feedstock for bio-energy production

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Dissertation submitted in fulfilment of the requirements for the degree *Magister in Chemical Engineering* at the Potchefstroom Campus of the North-West University

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May 2014

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Abstract

The suitability of water hyacinth (*Eichornia crassipes*) as a viable feedstock for renewable energy production was investigated in this project. Water hyacinth used in this study was harvested from the Vaal River near Parys in the northwest region of the Free State province, South Africa (26°54'S 27°27'E). The wet plants were processed in the laboratory at the North-West University by separating the roots from the leaves and the stems, thus obtaining two separate water hyacinth feedstock.

Characterisation of the feedstock showed that the stems and leaves are more suitable for bio-energy production than roots, due to the higher cellulose and hemicellulose content and very low lignin content of the stems and leaves. Water hyacinth was evaluated as feedstock for the production of bio-ethanol gel, bio-ethanol, bio-oil and bio-char. The recovery of water from the wet plants for use in bio-refining or for use as drip-irrigation in agriculture was also investigated.

Cellulose was extracted from water hyacinth feedstock to be used as a gelling agent for the production of ethanol-gel fuel. A yield of 200 g cellulose/kg dry feedstock was obtained. The extracted cellulose was used to produce ethanol-gel with varying water content. The gel with properties closest to the SANS 448 standard contained 90 vol% ethanol and 10 vol% water, with 38 wt% cellulose.

This gel was found to ignite readily and burn steadily, without flaring, sudden deflagrations, sparking, splitting, popping, dripping or exploding from ignition until it had burned to extinction, as required by SANS 448. The only specifications that could not be met were the viscosity (23,548 cP) and the high waste residue (32 wt%) left after burning. The other major concern is the extremely high costs involved with the manufacturing of ethanol-gel from water hyacinth cellulose. It can be concluded that ethanol-gel cannot be economically produced using water hyacinth as feedstock.

Chemical and enzymatic extraction of water from the feedstock, which is stems and leaves or roots, showed that the highest yield of water was obtained using a combination of Celluclast 1.5 L, Pectinex Ultra SP-L and additional de-ionised water. A yield of 0.89 ± 0.01 $g_{water}/g_{water\ in\ biomass}$ was realised. This is, however, only 0.86 wt% higher than the highest yield obtained (0.87 ± 0.01 $g_{water}/g_{water\ in\ biomass}$) using only Pectinex Ultra SP-L and de-ionised water. It is recommended to use only Pectinex Ultra SP-L and de-ionised water at a pH of 3.5 and a temperature of 40°C. Using one enzyme instead of two reduces operating costs and simplifies the chemical extraction process.

The extracted water, both filtered and unfiltered, was not found to be suitable for domestic use without further purification to reduce the total dissolved solids (TDS), potassium and manganese levels. Both the unfiltered and filtered water were, however, found to be suitable for industrial and agricultural purposes, except for the high TDS levels. If the TDS and suspended particle level can be reduced, the extracted water would be suitable for domestic, industrial and agricultural use.

The potential fermentation of the sugars derived from the water hyacinth, using ultrasonic pretreatment, was investigated. Indirect ultrasonic treatment (ultrasonic bath) proved to be a better pretreatment method than direct sonication (ultrasonic probe). The optimum sugar yield for the ultrasonic bath pretreatment with 5% NaOH was found to be 0.15 g sugar/g biomass (0.47 g sugar/g available sugar) using an indirect sonication energy input of 27 kJ/g biomass. The optimum sugar yield is lower than those reported in other studies using different pretreatment methods. Theoretically a maximum of 0.24 g ethanol can be obtained per g available sugar. This relates to an ethanol yield of 0.08 g ethanol/kg wet biomass. The low yield implies that ethanol production from water hyacinth is not economically feasible.

The production of bio-oil and bio-char from water hyacinth through thermochemical liquefaction of wet hyacinth feedstock was investigated. An optimum bio-char yield of 0.55 g bio-char/g biomass was achieved using an inert atmosphere (nitrogen) at 260°C and the stems and leaves as feedstock. With the roots as feedstock a slightly lower optimum yield of 0.45 g bio-char/g biomass was found using a non-reducing atmosphere (carbon monoxide) at 280°C. The bio-oil yield was too low to accurately quantify.

As water is required during thermochemical liquefaction, it was found unnecessary to dry the biomass to the same extent as was the case with the pretreatment and fermentation of the water hyacinth, making this a more feasible route for biofuel production. Bio-char produced through liquefaction of roots as the feedstock and leaves and stems as the other feedstock had a higher heating value (HHV) of 10.89 ± 0.45 MJ/kg and 23.31 ± 0.45 MJ/kg respectively. Liquefaction of water hyacinth biomass increased the HHV of the feedstock to a value comparable to that of low grade coal. This implies a possible use of water hyacinth for co-gasification.

The most effective route for bio-energy production in the case of water hyacinth was found to be thermochemical liquefaction (12.8 MJ/kg wet biomass). Due to the high production costs involved, it is recommended to only use water hyacinth as a feedstock for biofuel production if no alternative feedstock are available.

Keywords: Enzymatic extraction, ethanol-gel, lignocellulosic pretreatment, thermochemical liquefaction, water hyacinth

Declaration

I, Cornelis Johannes Schabort, hereby declare to be the sole author of the report entitled:

Evaluation of suitability of water hyacinth as feedstock for bio-energy production

For the fulfilment of the requirements for the degree of Master of Engineering in the School of Chemical and Minerals Engineering of the North-West University, Potchefstroom Campus.

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Cornelis Johannes Schabort

Potchefstroom

30 April 2014

Acknowledgements

"Zwei Stützen im Leben brechen nie, Arbeit und Gebet heißen sie."

The author wishes to gratefully acknowledge and deeply express his appreciation to the following people for their role during the course of this project:

- My heavenly Father who has blessed me beyond measure. Without Him I would never have been able to even complete a single page of this study.
- Professor Sanette Marx and Dr. Idan Chiyanzu. Without their expert guidance, critical evaluation of this work and inspiration during every stage of this study, this dissertation would never have been possible.
- Messrs. Thys Kühn, Cornie van Tonder and Dirk Uys, as well as Miss Megan Nagel, for their assistance and help during this project.
- All the personnel of the School of Chemical and Minerals Engineering who were always willing to assist.
- Mr. Vincent Delcour for his guidance during my time as process engineer at Natref.
- My family for their love and their support throughout my studies.
- All my friends, for the moral support.

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CHAPTER 1

INTRODUCTION

1.1 General

In this chapter a preface to the research study is presented. A motivation for research on renewable energy is given in Section 1.2 with a specific focus on the utilisation of water hyacinth as feedstock in the production of renewable bio-energy. The objectives of the study are listed in Section 1.3. The project scope, outline and description of the contents of this dissertation are presented in Section 1.4.

1.2 Background and motivation

The depletion of fossil fuel reserves and the increasing awareness of greenhouse gas emissions act as the primary driving force for finding alternative renewable energy sources. With oil, coal and gas predicted to peak in 46, 57 and 22 years respectively (Greene *et al.*, 2006; Thieleman *et al.*, 2007; Maggio & Cacciola, 2012), and an integrated study by Valero & Valero (2010) predicting an overall peak production of fossil fuels to occur around 2029, the search for a sustainable solution to the worldwide energy crisis is of the utmost importance.

Solar energy, wind energy, hydroelectricity and biofuels should all be critically evaluated, as the use of alternative energy sources are not without limitations and challenges. While solar energy, wind energy and hydroelectricity primarily address the generation of electrical power, the production of biofuels from biomass provides a very promising alternative for fossil derived liquid fuels (Demirbas, 2009a).

The major challenge related to the utilisation of biomass for biofuels, however, is the availability of the biomass. Not only should the environmental impact of feedstock production be considered, but also land and water utilisation, as well as the notorious food-versus-fuel debate (Dalai *et al.*, 2010). The ideal feedstock for biofuels production should thus ensure food security, as well as sustainability in terms of land utilisation and water consumption. Over and above existing feedstock, unconventional feedstock should also be considered, including alternative plants and organic waste.

Water hyacinth, *Eichornia crassipes*, was identified as a potential source of biomass for the production of renewable bio-energy. Water hyacinth is a noxious weed, rapidly depleting water bodies of nutrients and oxygen (Ganguly *et al*., 2011). Its fast spread and congested growth lead to severe problems with regards navigation, irrigation and power generation (Malik, 2006). Over and above the adverse effect water hyacinth has on fauna and flora, the high evapotranspiration of these plants also negatively impacts the global water crisis (Ganguly *et al*., 2011).

As water hyacinth is a weed, it does not have a direct impact on food security, and since these weeds should be eradicated from our natural water systems, the removed plant material could possibly be utilised for biofuels production. Possible products that can be manufactured from water hyacinth include bio-ethanol, biogas, compost and ethanol-gel. Other options include the utilisation of water hyacinth as phytoremediation agent and animal fodder.

The research problem can be summarised as follows:

- A sustainable solution is required to address the worldwide energy crisis.
- Biofuels, as an alternative, sustainable fuel, require biomass as feedstock that does not compete with land, water or food. Water hyacinth, as a weed, meets these criteria.
- As water hyacinth should be removed from natural water systems, the feasibility of the removed water hyacinth as a potential biomass feedstock should be considered.

This study will compare the various energy applications using water hyacinth as feedstock, focussing on energy yield as a function of input costs. The biofuels that will be compared include bio-ethanol, bio-char, as well as ethanol-gel.

1.3 Objectives of study

A research project was conducted to determine the optimum utilisation of water hyacinth as biomass feedstock in renewable energy production. The product yield and product quality of each alternative energy product and technology utilised, will be investigated.

The objectives of this study are:

a) To conduct a detailed chemical characterisation of the selected water hyacinth.

b) To conduct an extensive literature survey regarding water hyacinth utilisation in renewable energy applications.

c) To investigate the various energy applications of water hyacinth in terms of product quality and yield.

d) Conduct a comparative study of the energy produced per unit mass of the water hyacinth.

1.4 Scope of dissertation

In order to achieve the above-mentioned objectives, the following scope is proposed. The background and motivation, as well as the objectives of the study, is formulated in Chapter 1. In Chapter 2 an overview of the current worldwide energy situation is presented in order to understand the drive for renewable energy. Water hyacinth is discussed in detail as possible biomass for biofuels production.

The subsequent chapters discuss the experimental apparatus and methods used, as well as the results and conclusions for the production of ethanol-gel and the extraction of water from the biomass (Chapter 3), the ultrasonic pretreatment of the water hyacinth (Chapter 4) and thermochemical liquefaction (Chapter 5).

Finally, in Chapter 6 conclusions and recommendations on the results of the study are listed.

CHAPTER 2

2. LITERATURE SURVEY

2.1 Introduction

In this chapter, a literature review on water hyacinth as feedstock for biofuels is presented. The current worldwide energy situation is shown in Section 2.2 with a critical discussion of nuclear energy in Section 2.3. Renewable energies are discussed in Section 2.4, with a specific focus on water hyacinth as feedstock for bio-energy production.

2.2 Current worldwide energy situation

According to the EIA's report on energy (EIA, 2013), the primary energy consumption worldwide is expected to increase by 0.2% per annum, resulting in an overall increase in consumption of 6% by 2040. Another study (BP Statistical Review of World Energy, 2013) showed that worldwide energy consumption increased by 5.6% in 2010 to 12,000 million tons oil equivalent. This is the highest recorded annual increase in energy consumption since 1973.

These studies both confirm that the world still relies heavily on fossil fuels to meet growing international energy demands. The negative aspects inherently related to the consumption of fossil fuels include the environmental impact of CO_2 emissions, the depletion of fossil fuel reserves, as well as the economic dependence on countries where political instability is prevalent (Maggio & Cacciola, 2012).

2.2.1 Fossil fuels

Fossil fuels in the form of oil, coal and natural gas remain the world's largest source of energy (EIA, 2013). These fossil fuels play a pivotal role in the generation of electricity, as well as in the production of transportation fuels chemicals. Eighty seven percent (87%) of the worldwide commercial energy needs is met by fossil fuel sources with 98% of all transportation fuels being derived from fossil fuel sources (Almeida & Da Silva, 2009; BP Statistical Review of World Energy, 2013).

2.2.1.1 Oil

Oil is the single biggest contributor to energy supply in the world, with a market share of 33.1%. In 2012, the worldwide oil supply reached a record level of more than 86 million barrels per day (BP Statistical Review of World Energy, 2013; Maggio & Cacciola, 2012), with 52.6% of this oil being produced by the four biggest oil producing countries, *i.e.* the United States of America (9.6%), Saudi Arabia (13.3%), the Russian Federation (12.8%) and China (5.0%). There has also been an annual growth in oil consumption of 0.9% (BP Statistical Review of World Energy, 2013).

Two kinds of oil can be distinguished, *i.e.* conventional (light hydrocarbons with a light to medium viscosity, which can be extracted from porous and permeable reservoirs, as well as natural gas liquids) and unconventional oil (heavy oil, oil sands and oil shale). The total proven conventional and unconventional oil reserves at the end of 2012, based on geological and engineering information, were calculated to be 1,67 billion barrels (BP Statistical Review of World Energy, 2013). This includes the Canadian oil sands, which contribute approximately 143,000 million barrels (9.4%) to the total oil reserves (Greene *et al.*, 2006).

Many studies have been undertaken to determine when peak oil production will occur. According to Maggio & Cacciola (2012) peak oil production will occur sometime between 2009 and 2021. Greene *et al.* (2006) anticipate severe constraints on oil production by 2023, while Aleklett *et al.* (2010b) have predicted a steep decline in oil production by 2030. A more conservative prediction by Valero & Valero (2010) showed that the point of peak oil production was already reached in 2008.

Given the current trend in oil consumption, all conventional oil reserves will be depleted within 46 years. A major changeover from conventional to unconventional oil is thus required. In order to meet the growing energy demand, the switch from conventional to unconventional oil should occur at a rate of 7 – 9% per annum before 2030 (Greene *et al.*, 2006).

2.2.1.2 Coal

Coal currently accounts for 23.9% of the world's primary energy demand, making it the second largest fossil fuel energy contributor (Maggio & Cacciola, 2012). There has been a worldwide growth in coal consumption of 2.5% in 2012, with the consumption in China alone growing by 6.1% (BP Statistical Review of World Energy, 2013).

Even though coal is not the largest fossil fuel energy contributor, it is globally the most abundant fossil fuel. The total proven coal reserves in 2012 amount to 860,938 million tonnes, with 75% of these reserves found in the United States of America (27.6%), Russia (18.2%), China (13.3%), Australia (8.9%) and India (7.0%). The total production of coal in 2012 amounted to 3,845 million tonnes, with the five biggest coal producing countries, *i.e.*, China (47.5%), the United State of America (13.4%), Australia (6.3%), Indonesia (6.2%) and India (6.0%), producing 79.4% of the world's coal (BP Statistical Review of World Energy, 2013).

The predicted coal peak production is expected to occur between 2042 and 2062 (Maggio & Cacciola, 2012), which is in line with the 2060 prediction of Valero & Valero (2010). Aleklett *et al.* (2010a) found that even if the recoverable coal reserves are twice the current reported volume, peak coal production will occur between 2030 and 2050. These predictions support the findings of Rutledge (2011), who has predicted that 90% of the total coal production would have taken place by 2070. Thielemann *et al.* (2007), on the other hand, have a much more optimistic outlook on coal production, with an expectation that there will be no problem with regards to coal supplies up to the year 2100.

2.2.1.3 Natural gas

The third largest fossil fuel source is natural gas with a share of 23.9% in the world's primary energy supply (Maggio & Cacciola, 2012). Similar to oil and coal, there has been growth in both the demand and supply of natural gas with consumption growing by 1.9% and production by 2.2% in 2012. The total proven natural gas reserves in 2012 amounted to 187.3 trillion m^3, with Iran (18%), Russia (17.6%) and Qatar (13.4%) making out 49% of these reserves, with the United States of America (20.4%) and Russia (17.6%) as the biggest producers of natural gas (BP Statistical Review of World Energy, 2013). Maggio & Cacciola (2012) predict a peak natural gas production in 2035, while Valero & Valero (2010) predict a more conservative peak year of 2023.

2.2.1.4 Conclusion

It can be concluded that fossil fuels are being depleted at a rapid rate. Peak production of oil is predicted to occur between 2008 and 2030, while the peak production of coal is expected to occur between 2020 and 2060. The predicted peak production of natural gas will occur between 2023 and 2035. This is in line with an integrated study by Valero & Valero (2010) that predicted an overall peak production of fossil fuels to occur in 2029.

2.3 Nuclear energy

In 2012 the world nuclear energy supply declined by 6.9% to 560.4 million tonnes oil equivalent. The main consumers, namely the United States (32.7%), France (17.2%) and Russia (7.2%), consume 57.1% of the available nuclear energy (BP Statistical Review of World Energy, 2013). The contribution of nuclear energy to the total world energy supply is, however, only 4.49% and is mainly in the form of electrical energy (Dittmar, 2012). In a study by Kahouli (2011) the total amount of nuclear energy supply is expected to increase by 73% to 4800 TWh by 2030. This is still a negligible amount considering the growing worldwide energy demand.

Furthermore, nuclear power has been dealt a blow with regards to public acceptance, following the Fukushima incident in Japan (Maggio & Cacciola, 2012). As a result of this catastrophe, many countries are re-evaluating the role of nuclear energy as a source of low-carbon electricity (REN21, 2011).

Even though nuclear power is not a fossil fuel based energy source, it cannot be classified as a renewable energy source, as the uranium supply is limited and non-renewable. Peak uranium production of between 98,000 and 141,000 tons is expected to occur in 2020, with a steep decline to between 68,000 and 109,000 tons per annum in 2035 (Dittmar, 2012). Similar to fossil fuels, uranium is also being depleted at a fast pace.

2.4 Renewable energy

From an environmental and energy supply point of view, the importance of renewable energy sources cannot be overemphasised, especially if it is taken into account that the peak production periods of fossil fuels and nuclear energy are 1 to 2 decades away (Demirbas, 2001). As the use of alternative energy sources are not without limitations and challenges, the various sources should be critically evaluated. As hydrogen should rather be seen as energy carrier than a primary fuel source (Maggio & Cacciola, 2012), hydrogen will not be considered under renewable energy sources.

2.4.1 Solar energy

Solar energy is by far the most abundant renewable energy resource available, with the amount of solar radiation reaching the earth being much higher than the global annual energy consumption.

According to Johansson *et al.* (2004) even the minimum technical potential of solar energy is 3 times higher than the primary energy demand.

Despite the recent decline in the cost of solar energy, it is still rather costly compared to conventional energy technologies. Various fiscal and regulatory incentives are a prerequisite for the successful implementation of solar energy (Kurdgelashvili *et al.*, 2012).

Solar energy mainly focuses on three areas, namely solar photovoltaics (PV), concentrated solar thermal power (CSP) and solar hot water/heating. The PV industry increased the global solar capacity by 10 GW, bringing the total capacity to 40 GW. This is quite remarkable if taken into account that the solar PV capacity worldwide was 0.7 GW in 1996 (REN21, 2011). In 2010 crystalline silicon-based PV cells accounted for 80% of all cells produced (Kurdgelashvili *et al.*, 2012).

Advances in CSP have been much slower than in the field of PV technology. The total installed CSP capacity in 2010 was 1.1 GW, with parabolic trough plants accounting for 90% of all CSP plants. Solar hot water/heating has, however, shown remarkable growth the last couple of years, reaching 185 GWh in 2010 (REN21, 2011).

Even though the total number of countries that have an installed solar power capacity in excess of 1 GW have grown to 7 (Germany, Spain, Japan, Italy, the United States of America, France and the Czech Republic), the contribution of solar power to the overall power supply worldwide is estimated at only 0.1% (BP Statistical Review of World Energy, 2013).

2.4.2 Wind energy

Wind power is an abundant, clean, renewable energy source, which is expected to increase in capacity to over 400 GW by 2014 (Sun *et al.*, 2012). The global wind power generating capacity grew from 160 GW in 2009 to 200 GW in 2010. This translates to 340 TWh or 1.6% of the total energy supply worldwide. China has overtaken the United States of America with regards to installed wind capacity in 2010. With a market share of 44% (88 GW), Europe remains the single largest regional market with regards to wind power (BP Statistical Review of World Energy, 2013).

Similar to solar energy, wind energy also requires some form of financial support to be viable, but to a lesser extent than with solar energy. It is noted that the price of wind energy is not that high if compared to the price of coal, gas or nuclear power, depending on the location (Milborrow, 2012). A major challenge with regards to wind power production, however, is the availability of land. Due to this limitation, offshore installations are seen as the future with regards to wind energy (Sun *et al.*, 2012). The cost of electricity from offshore facilities are roughly double that of onshore installations (Milborrow, 2012). Esteban & Leary (2012) have shown that 7% of the total worldwide electricity production could come from these offshore facilities by 2050.

2.4.3 Hydroelectricity

There has been growth in hydroelectric global supply every year since 2003, bringing the total global output to 831.1 million tonnes of oil equivalent in 2012. China (23.4%), Brazil (11.4%), Canada (10.4%) and the United States of America (7.6%) are the four biggest consumers of hydroelectricity (BP Statistical Review of World Energy, 2013).

The majority of hydroelectricity is produced using dams, but run-of-the-river electricity is also a feasible option (Delucchi & Jacobson, 2011). The production of hydroelectricity shows great potential, especially in developing countries. Not only is the operating and fuel costs extremely low, but the greenhouse gas emissions are negligible (Da Silva *et al.*, 2010). The hydropower capacity is expected to increase to 4248 TWh by 2030 (Haddad, 2011).

2.4.4 Biofuels

Energy derived from biomass contributes 10.4% to the world's primary energy supply and contribute 77.4% of the world's renewable energy supply (Kamarudin *et al.*, 2011). While solar energy, wind energy and hydroelectricity primarily address the generation of electrical power, the production of biofuels from biomass provides a very promising alternative for fossil fuels derived liquid fuels (Demirbas, 2009a). According to Bart *et al.* (2011) biofuels currently make up 1.5% of the world's transportation fuel. This figure is expected to increase to almost 7% in 2030 (Bae & Cha, 2011).

There was a decline in world biofuels production of 0.4% in 2012, which is the first decline since 2000. While global ethanol output declined by 1.7%, biodiesel production increased by 2.7%. Almost 70% of the worldwide biofuels production occurred in the United States of America (45.4%) and Brazil (22.5%). The only other countries worth mentioning is Germany (4.8%), Argentina (3.8%) and France (3%), with the rest of the world lagging considerably with regards to the overall biofuels production (BP Statistical Review of World Energy, 2013).

The main biofuels are bioethanol and biodiesel, which can be used as liquid fuel in petrol and diesel engines respectively. Mabee *et al.* (2009) found the total bioethanol production in 2008 to be 66.6 billion litres, while the biodiesel production was 10.9 billion litres. There has been considerable growth in these production figures, considering the bioethanol production in 2010 of 85 billion litres and that of biodiesel of 21 billion litres (BP Statistical Review of World Energy, 2013). The OECD-FAO (2011) agricultural outlook reported a slightly higher bioethanol production (99.5 billion litres), but a slightly lower biodiesel production (19.8 billion litres) figure.

These increases can be explained by government directives with regards to biofuels. In 2007 the United States have set a target of 136 billion litres of biofuels production by 2022, which is almost double the worldwide production of 2008 (Behnam *et al.*, 2011), while Europe has called for 10% of all transportation fuels to be biofuels by 2020 (Di Serio *et al.*, 2012). This might be a difficult feat to achieve, as the 2020 production of bioethanol and biodiesel is predicted to be 155 billion litres and 42 billion litres respectively (OECD-FAO, 2011).

Other biofuels include biogas, biomethanol, bio-ethers, biohydrogen, as well as pure vegetable oil (Bart *et al.*, 2011). According to Demirbas (2009b) biofuels have many advantages over traditional fossil fuels, including increased energy security, a reduction in greenhouse gases, an increased independence of foreign countries, as well as job creation and improved socioeconomic conditions in rural areas. A distinction can be made between first and second generation biofuels. First generation biofuels utilise sugar, starch or vegetable oil as substrate, including wheat, barley, corn, potato, sugar beet, sugar cane, rapeseed, soybeans, sunflower, palm and coconut (Nigam & Singh, 2011). Due to the food-versus-fuel debate, first generation biofuels are not sustainable as an increase in the production of first generation biofuels will have a negative impact on the production of vital food commodities (Dalai *et al.*, 2010).

Second generation biofuels, on the other hand, focus on non-food commodities as feedstock. Only 0.1% of all biofuels are currently second generation biofuels, but to avert the challenges related to first generation biofuels, there is justification to pursue these new technologies. As soon as second generation biofuels technologies are commercially viable, government policies with regards to the environment and energy security may favour these novel technologies above established first generation biofuels production (Mabee *et al.*, 2010).

Second generation biofuels feedstock specifically comprise of by-products, wastes and dedicated feedstock (Mabee *et al.*, 2010). The lignocellulosic feedstock utilised in the production of second generation bioethanol include wheat straw (Esbensen *et al.*, 2010), rice straw (Baruah & Hiloidhari, 2011), barley straw (Ballesteros *et al.*, 2011), rapeseed straw (Cara *et al.*, 2011), *Miscanthus* (De Corato *et al.*, 2011), poplar (Bai *et al.*, 2012), willow (Dennis *et al.*, 2010), sugarcane bagasse (González-César *et al.*, 2009) and sweet sorghum bagasse (Faulstich *et al.*, 2012), to name but a few. Non-food related feedstock in the production of biodiesel include brown grease, microalgae, macroalgae, oleaginous microorganisms, as well as various non-edible oils like those derived from *Jatropha*, the sandbox tree and the sea mango tree (Bart *et al.*, 2011).

2.4.5 Water hyacinth as biofuel

Another viable second generation biofuels feedstock is water hyacinth, *Eichhornia crassipes* (Chatterjee *et al*., 2012). The water hyacinth is a tropical, monocotyledonous freshwater aquatic plant that can be found in lakes, rivers and swamps in countries situated between 40°N and 40°S (Malik, 2007). The plants can grow up to a meter in height. Air filled sacs, which are located in the stem and leaves, assist in keeping the plant afloat (Chatterjee *et al*., 2012).

Its fast spread and congested growth lead to severe problems with regards to navigation, irrigation and power generation (Malik, 2007). The noxious weed rapidly depletes water bodies of nutrients and oxygen. The high density of water hyacinth (more than 60 kg/m^2) negatively impacts the environment, human health and economic development (Holst *et al.,* 2005). Over and above the adverse effect water hyacinth has on fauna and flora, the high evapotranspiration of these plants also negatively impacts the global water crisis (Chatterjee *et al*., 2012). Eradication of the invasive water hyacinth has been a challenge since its introduction to South Africa around the beginning of the 20th century. Water hyacinth seeds are long-lived and remain viable for more than 2 decades (Coetzee *et al.*, 2011).

From a renewable energy point of view, water hyacinth presents an excellent source of biomass for the production of renewable bio-energy. Various investigations have been undertaken to study the potential suitability of water hyacinth for bio-ethanol production, biogas production, compost production, as well as the utilisation of water hyacinth as phytoremediation agent and animal fodder (Chatterjee *et al*., 2012).

2.4.5.1 Moisture content of water hyacinth

One of the major challenges with regards to water hyacinth as a biofuel feedstock is the high water content, being as high as 95 wt% (Nigam, 2002). Water extraction is thus an essential process step in decreasing the moisture content of water hyacinth prior to the production of biofuels. The extracted water can possibly be utilised as an additional source of water.

According to the UN, water utilisation has been increasing at double the rate of the global population growth during the last 100 years (FAO, 2007). The availability of water for domestic, industrial and agricultural application is a growing worldwide concern, with an increasing number of areas being chronically short of water. As the 30th driest country in the world, with an average rainfall of just 450 mm per annum, South Africa faces the same water scarcity problem as the rest of the world (Ainslie & Palmer, 1997).

Previous studies on the extraction of water from plant material have shown excellent results with regards to water extraction from cacti (Bothma *et al.*, 2013). Similar to water hyacinth, certain South African cacti species, such as *Cereus jamacura*, *Opuntia ficus-indica*, *Opuntia imbricata* and *Echinopsis spachiana*, are classified as invasive plants and declared weeds according to the South African Conservation of Agricultural Resources Act (South Africa, 1983; Henderson, 2001). Both water hyacinth and these cacti species are targeted for control due to their serious environmental impact, including higher usage of water, blockage of water passages, erosion, as well as the reduction in the specific environment's biodiversity.

Mechanical methods used for recovering juice from fruit include chopping, pressing, diffusion and centrifugal processes. The purpose of these methods is to separate the liquid phase from the solid phase (Barta *et al*., 2002). Despite the simplicity, low maintenance and low capital input required the utilisation of a hydraulic cold press and pressing with rollers to extract water from cacti has been proven to not be very efficient (Bothma *et al.*, 2013).

Juicing using a juicer or an extractor produces a murky liquid product that contains no suspended solids (Barrett *et al*., 2004). Juicing by rotary methods increases the amount of polysaccharides (including pectin and cellulose) extracted from the pulp to the liquid product (*Barta* et al., 2002).

Chemical extraction techniques, on the other hand, are also well documented in literature and readily available. The combined synergetic use of pectinase and cellulase further increases the extraction yield of the juice from the pulp (Dörrich, 1996). In a study by Santhanam *et al*. (1994) the addition of cellulase and pectinase increased the recovery of juice from pineapples by up to 14%. Acar *et al*. (2001) did a similar study and found that pectinase increased juice yield from carrots by 17.7%. Furthermore, surfactants also play an important role in breaking down cellulose in plants and fruit. In a study by Li *et al*. (2011) it was shown that a surfactant can increase the hydrolysis of cellulose at high rotation speeds. Bothma *et al.* (2013) found that mechanical methods proved to be unsuccessful and a maximum yield of 7 wt% was obtained by using a juicer. Chemical extraction methods proved to be more efficient. Celluclast, Pectinex Ultra SP-L and Tween 80 were added to cacti pulp at different process conditions. The optimum process conditions for the highest water yield were obtained as follows:

- Celluclast 1.5 L: 55 wt% (T = 40°C and pH = 5.5)
- Pectinex Ultra SP-L: 55 wt% (T = 40°C and pH = 3.5)
- Tween 80: 50 wt% (T = 40°C and pH = 3.5)

It is thus expected that cellulase, pectinase and surfactants will improve the water extraction from water hyacinth. Cellulase and pectinase are both enzymes which are generally used in food processes where juice is extracted. The surfactant, on the other hand, is a known polysorbate which is used in a variety of industries, including healthcare and detergents.

2.4.5.2 Dry composition of water hyacinth

The average cellulose, hemicellulose, lignin and crude protein content of the dry solids found in the water hyacinths is shown in Table 1.

Table 1: Chemical analysis of water hyacinths (dry basis wt%)

Study	**Cellulose**	**Hemicellulose**	**Lignin**	**Crude protein**
Nigam (2002)	18.2	48.7	3.5	13.3
Cen *et al.* (2010)	28.9	30.8	4.6	21.0
Murugesan & Radhika (2012)	25.0	35.0	10.0	9.0
Abdelhamid & Gabr (1991)	19.5	33.4	9.3	20.0
Desai *et al.* (1993)	17.8	43.4	7.8	11.9
Banerjee *et al.* (1991)	25.6	18.4	9.9	16.3
Fujita *et al.* (2008)	19.7	27.1	Not analysed	Not analysed
Ghosh *et al.* (2009)	18.4	49.2	3.6	12.6
Ma *et al.* (2010)	18.2	29.3	2.8	Not analysed
Luo *et al.* (2011)	26.1	26.8	6.3	18.0
Danon *et al.* (2008)	46.7[a]		27.7	Not analysed
Abidin *et al.* (2011)	40.2[a]		6.5	Not analysed

[a] *Combined value of cellulose and hemicellulose*

It can be seen that the composition of the water hyacinth varies considerably. Gunnarsson and Petersen (2007) explained in their study that the chemical composition of the water hyacinths is strongly dependent on its environment.

The average cellulose, hemicellulose and lignin content of other biomass feedstock are shown in Table 2.

Table 2: Chemical analysis of biomass feedstock (adapted from Rosendahl *et al.*, 2011)

Biomass feedstock	**Cellulose**	**Hemicellulose**	**Lignin**
White poplar	49.0	25.6	23.1
European birch	48.5	25.1	19.4
White willow	49.6	26.7	22.7
White spruce	44.8	30.9	27.1
Monterey pine	41.7	20.5	25.9
Douglas fir	42.0	23.5	27.8
Corn stover	37.1	24.2	18.2
Sugarcane bagasse	39.0	24.9	23.1
Wheat straw	44.5	24.3	21.3

Compared to other biomass feedstock hyacinth has a higher hemicellulose content and a lower cellulose and lignin content. The main types of energy that can be produced from lignocellulose are shown in Figure 1 (Menon & Rao, 2012).

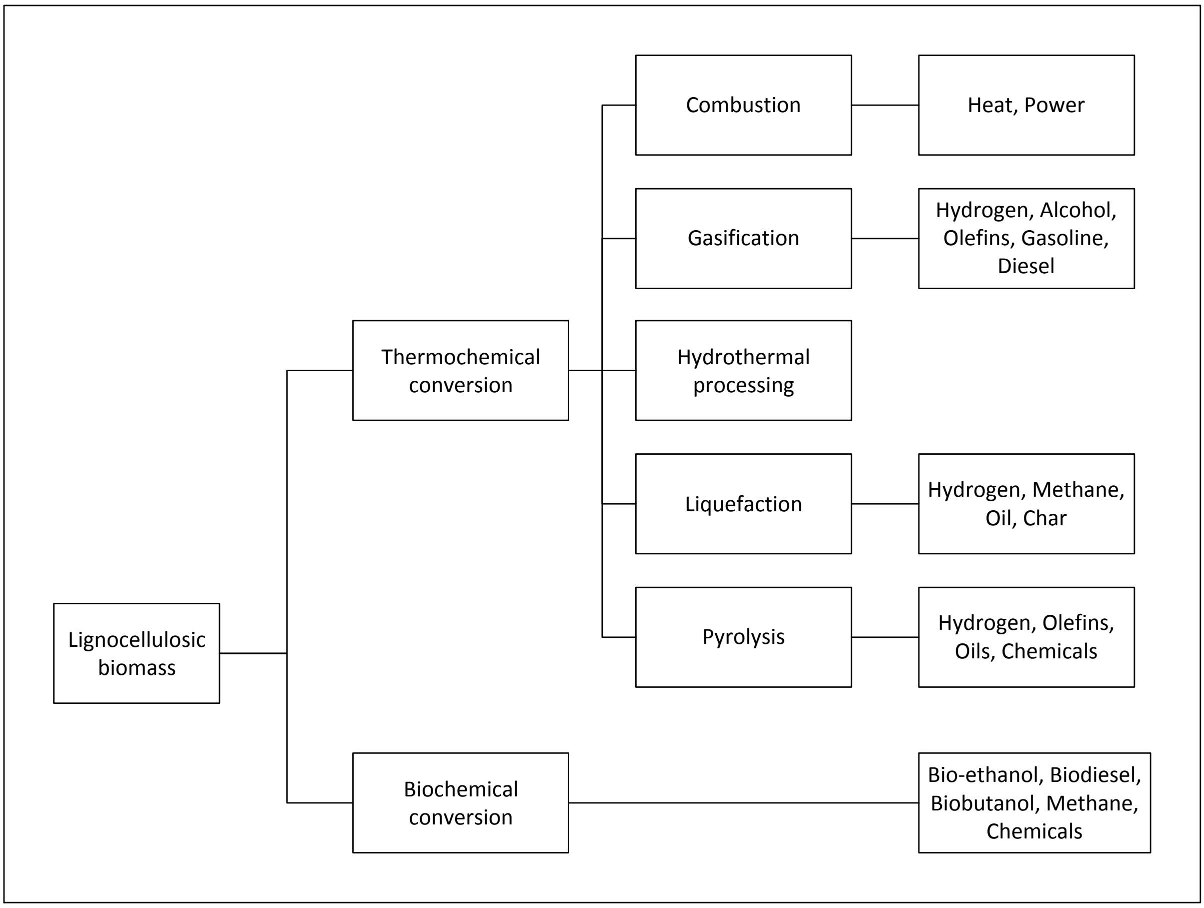

Figure 1: Thermochemical and biochemical processing of lignocellulosic biomass (adapted from Menon & Rao, 2012)

2.4.5.3 Bio-ethanol from water hyacinth

Lignocellulosic material is an abundant and cheap feedstock available for bio-ethanol production (Hahn-Hägerdal & Olsson, 1996). Dried water hyacinths consist mainly of hemicellulose (18.4 – 49.2%), cellulose (17.8 – 28.9%) and lignin (2.8 – 10%), depending on where the plants were harvested. The high hemicellulose and crude protein content make it an ideal feedstock for lignocellulosic fermentation. The fermentation of lignocellulosic hydrolysates, however, is much more complex than the fermentation of conventional sugars and starches, due to the presence of cellulose, hemicellulose and lignin (Mabee *et al.*, 2011).

Cellulose consists of D-glucose monomers linked together with β-1,4 glycosidic linkages to form a long, unbranched chain (Kargi & Shuler, 2008). Hemicellulose is a heterogeneous compound, consisting of five sugars, *i.e.* D-glucose, D-galactose, D-mannose, D-xylose and L-arabinose (Mabee *et al.*, 2011). The third most abundant natural polymer, lignin, consists of phenylpropane units. Three aromatic alcohols, *i.e.* p-coumaryl, coniferyl and sinapyl alcohols form the precursors of these phenylpropane units (Buranov & Mazza, 2008).

Pretreatment of the hyacinth can be done using pretreatment methods that fall into four different categories, namely physical (milling, extrusion, microwave or freeze pretreatment), chemical (acid, alkaline, ionic liquid, organosolv or ozonolysis), physico-chemical (steam explosion, ammonia fibre explosion, CO_2 explosion, liquid hot water, wet oxidation) and biological pretreatment. Each of these methods has distinct advantages to increase the specific area of the biomass. The choice of pretreatment method, however, relies heavily on the type of biomass (Ardjmand *et al.*, 2013). Various pretreatment methods are compared in Table 3, showing the advantages, disadvantages and drawbacks of the methods.

Table 3: Comparison of different pretreatment methods related to lignocellulosic material (Ardjmand *et al.*, 2013)

Pretreatment method	**Advantages**	**Disadvantages**	**Drawbacks**
Physical pretreatment	Highly effective decrystallisation of cellulose. Low formation of inhibitor compounds.	Poor removal and solubilisation of hemicellulose. Poor removal of lignin.	High energy consumption.
Acid pretreatment	Highly effective removal and solubilisation of hemicellulose. Effective lignin removal.	Poor decrystallisation of cellulose. High formation of inhibitor compounds.	Corrosion of equipment. Degrading of sugars. Pretreated slurry requires neutralisation.
Alkaline pretreatment	Highly effective lignin removal. Effective removal and solubilisation of hemicellulose.	Poor decrystallisation of cellulose. Some formation of inhibitor compounds.	Long pretreatment residence time required. Pretreated slurry requires neutralisation.
Ionic liquid	Highly effective decrystallisation of cellulose. Effective removal and solubilisation of hemicellulose. Effective lignin removal.		Ionic liquid is quite expensive.
Organosolv	Highly effective removal and solubilisation of hemicellulose. Highly effective lignin removal.		High cost involved with recycling and recovering of solvent.
Ozonolysis	Highly effective lignin removal.	Poor removal and solubilisation of hemicellulose.	Large ozone inventory required. Process expensive.
Steam explosion	Highly effective removal and solubilisation of hemicellulose.	Poor decrystallisation of cellulose. High formation of inhibitor compounds.	Lignin-carbohydrate matrix not completely disrupted. Toxic component as by-product.
AFEX	Highly effective decrystallisation of cellulose. Highly effective lignin removal. Effective removal and solubilisation of hemicellulose.	Some formation of inhibitor compounds.	High pressure required. Not suitable for biomass with high lignin content. Ammonia is expensive.
CO_2 explosion	Highly effective removal and solubilisation of hemicellulose.	Poor decrystallisation of cellulose. Poor removal of lignin.	High pressure required. Low effect on cellulose and lignin.
Wet oxidation	Highly effective removal and solubilisation of hemicellulose. Highly effective lignin removal. Effective decrystallisation of cellulose.		Oxygen and catalyst are expensive.
Liquid hot water	Highly effective removal and solubilisation of hemicellulose.	Some formation of inhibitor compounds.	pH control requires addition of alkaline. High temperature required.
Biological	Highly effective lignin removal. Effective decrystallisation of cellulose.		Low rate of hydrolysis. High residence time required. Specific growth conditions required.

Ultrasonication alters the biomass structure by inducing cavitations and size reduction due to the collision of particles. Abidin *et al.* (2011) reported a sugar yield of 132.96 mg sugar/g dry matter using ultrasound (100% power, 20 minutes, 10 w/v% biomass loading, direct probe). Residence times in excess of 20 minutes (high power) lead to a decrease in sugar yields, while longer times were required for optimum sugar yield in the case of a low power setting. This trend is consistent with results obtained using other biomass such as palm oil and corncob (Abidin *et al.*, 2011). The combined chemical and physical treatment systems allow the hemicellulose to dissolve and provide sufficient alteration of the lignin structure to improve access for the hydrolytic enzymes. The lignin is removed using either enzymatic, acid or alkali hydrolysis. The resulting 5- and 6-ring sugars are then fermented to ethanol (Chatterjee *et al.*, 2012).

The yeast, *Saccharomyces cerevisiae*, is most frequently used for fermentation of hydrolysates to ethanol. However, the wild-type *S. cerevisiae* are able to ferment a limited range of C-6 sugars only. *Zymomonas mobilis* is added to assist with fermentation of pentose sugars such as xylose and arabinose (Goshadrou *et al.*, 2011).

Three main groups of inhibitors that form during the hydrolysis of lignocellulosic substrates are weak acids, furan derivatives, as well as phenolic compounds. The presence of these inhibitors in the fermentation broth will reduce the efficient conversion of sugars to ethanol by the microorganisms (Hahn-Hägerdal & Palmqvist, 2000). The ethanol yields for various previous studies are shown in Table 4.

Table 4: Ethanol yield obtained during various studies using different fermentation strains

Ethanol yield ($g_{ethanol}/g_{biomass}$)	**Fermentation strain**	**Study**
0.14	*S. cerevisiae*	Fujita *et al.* (2008)
0.17	*E. coli*	Fujita *et al.* (2008)
0.19	*C. shehatae*	Chatterjee *et al*. (2012)
0.19	*S. cerevisiae*	Ma *et al.*(2010)

2.4.5.4 Bio-char, bio-oil and bio-gas from water hyacinth

Hydrothermal liquefaction has been proven to be an ideal process to convert wet biomass into gaseous, liquid and solid fuels. This process is usually executed at temperatures ranging from 280 to 370°C and pressures ranging from 10 to 25 MPa (Rosendahl *et al.*, 2011). One of the advantages of hydrothermal liquefaction above pyrolysis is that no energy consuming drying step is required for the biomass (Bridgwater *et al.*, 1999).

During liquefaction the feedstock is broken down into smaller fragments, which are then degraded by dehydration, dehydrogenation, deoxygenation and decarboxylation to form simple compounds

(Demirbas, 2000). These compounds are then rearranged by condensation, cyclization and polymerization to form the main products of hydrothermal liquefaction, namely bio-oil, with a relatively high heating value, bio-char, as well as water-soluble substances and bio-gas (Rosendahl *et al.*, 2011).

There are numerous studies that were performed on the liquefaction of various other types of biomass, as shown in Table 5.

Table 5: Previous studies on the thermochemical liquefaction of biomass

Feedstock	**Catalyst**	**Observations**	**Study**
Cellulose	HCl, NaOH	The bio-oil composition depends on the acidity of the liquefaction mixture. The bio-oil consisted mainly of 5-(Hydroxymethyl)furfural under acidic and neutral conditions. Under alkaline conditions the bio-oil mainly consisted of $C_{2–5}$ carboxylic acids.	Tan & Yin (2012)
Micro-algae (*Scenedesmus* and *Spirulina*)	None	Hydrothermal liquefaction is preferred above pyrolysis in cases where the initial moisture content of the biomass is in excess of 80%.	Blazina *et al.* (2012)
Cypress	None	Higher temperatures led to a decrease in bio-oil production, but an increase in bio-gas. Bio-oil yield decreased and bio-char yield increased with a longer reaction time.	Li *et al.* (2012)
Cornelian cherry stones	None	At a lower residence time there was an increase in the total bio-oil yield. With an increase in temperature, there was also an increase in the heating values of the bio-oil.	Akalin *et al.* (2012)
Micro-algae (*Spirulina platensis)*	Na_2CO_3, $Ca_3(PO_4)_2$, NiO	Using Na_2CO_3 as catalyst was found to decrease bio-gas yields if compared to non-catalytic liquefaction. NiO and $Ca_3(PO_4)_2$, on the other hand, favoured bio-gas yields. Na_2CO_3 was found to be the only catalyst that produced similar bio-oil yields than with non-catalytic liquefaction, but at lower temperatures and residence times.	Das *et al.* (2012)
Micro-algae (*Dunaliella tertiolecta*)	None	A synergistic effect was found using ethanol and water during the direct liquefaction process. A maximum bio-oil yield of 64.68% was obtained at 320°C and a residence time of 30 minutes. The liquid mixture was 40% (v/v) ethanol.	Chen *et al.* (2012)
Sawdust	NaOH, H_3PO_4, H_2SO_4	The sawdust was effectively liquefied in the compressed ethanol. A conversion of 97.8 wt% was obtained at 250 °C and 1 hour residence time using glycerol and ethanol as solvent. A higher yield was obtained with acidic catalysts than with base catalysts.	Dai *et al.* (2012)
Cellulose	None	Cellulose was successfully liquefied using hot compressed water. Optimum bio-oil yields were obtained at 250°C, while bio-gas is favoured at 350°C.	Chen *et al.* (2012a)
Marine brown algae (*Sargassum patens)*	Na_2CO_3	Optimum bio-oil yield is obtained at 340°C, with a decrease in bio-char and bio-oil yield and an increase in bio-gas yield beyond this point. The addition of Na_2CO_3 decreased the bio-char and bio-oil yield and increased the bio-gas yield.	Chen *et al.* (2012b)

A summary of the influence of operating conditions on the thermochemical liquefaction process is summarised in Table 6.

Table 6: Influence of operating conditions on the thermochemical liquefaction process

Operating variable	**Influence on thermochemical liquefaction**
Temperature	The oil yield will increase with an increase in the operating temperature. There is, however, a temperature where the oil yield will either start to decline or level off (Barnard, 2009). The increased oil yield is explained by improved separation between the oil and aqueous phases at elevated temperatures (Koguchi *et al.,* 1987). With an increase in bio-oil yield, however, there is a decrease in bio-char yield (Bolat *et al.*, 2000; Etcheverry & Xu, 2008).
Reaction atmosphere	The hydrogen content of the biomass has a significant impact on the choice of reaction atmosphere. If the biomass does not have sufficient hydrogen content for internal hydrogen-shuttling, a reducing atmosphere is required for optimum liquefaction yields (Barnard, 2009).
Pressure	Operating pressure does not have a significant impact on thermochemical liquefaction (Barnard, 2009).
Holding time	The influence of the holding time is dependent on the biomass feed stock, the reaction atmosphere, as well as the operating temperature (Barnard, 2009).
Solvent	The liquefaction solvent has an effect on the thermochemical process and the choice of solvent is dependent on the biomass feed stock (Barnard, 2009).
Catalyst	The liquefaction process is influenced by both the type of catalyst and the catalyst load (Barnard, 2009).

In a study done by Lu *et al.* (2011) on water hyacinth bio-oil yields of 10.3 – 12.6 wt% and bio-char yields of 42.7 – 48.9 wt% were obtained. The optimum bio-oil and bio-char temperatures were found to be 350°C and 300°C respectively. Another study done on water hyacinth showed a bio-oil yield of 26 wt% at a temperature of 350°C (Butner, 1988).

2.4.5.5 Ethanol-gel from water hyacinth

The liquid fuel most commonly used for domestic lighting, heating and cooking in rural areas is paraffin, also called kerosene. The choice of fuel is based on a combination of factors, including affordability, accessibility, cost involved to obtain the energy and the cost of the appliances (Albertyn *et al.*, 2012). Paraffin is, however, in many cases the main cause of loss of life and property in these rural areas (Alstad *et al.*, 2005). The paraffin used in some domestic applications is heated above its flash point and during an accident can increase the temperature inside a typical low-income house to above 400°C within 30 seconds (Lloyd & Visagie, 2007).

Ethanol-gel is an excellent alternative fuel to paraffin. Ethanol-gel is a colloid comprised of ethanol and a thickener additive, which can be carbopol or carboxymethyl cellulose (Bizzo *et al.*, 2004). The risk of rapid spreading fires is reduced considerably due to the high viscosity of ethanol-gel. The other advantages of ethanol-gel include a reduction in polluting emissions, no odour, as well as sufficient energy for both cooking and heating. In some cases, however, the cooking time has been found to be much slower with ethanol-gel than with normal paraffin (Albertyn *et al.*, 2012).

Previous studies on the higher heating values and burn times of commercial ethanol-gels, as well as laboratory synthesised ethanol-gels, are shown in Table 7.

Table 7: Burn times and higher heating values of ethanol-gels

Ethanol-gel	**Higher heating value (MJ/kg)**	**Burn time (seconds)**	**Study**
Sun gel	18.7	Not analysed	Lloyd & Visagie, 2007
Enviro-Heat	18.6	Not analysed	Lloyd & Visagie, 2007
Bio-Heat gel	17.7	Not analysed	Lloyd & Visagie, 2007
Prickly Pear	17.9	122	Smit, 2010
Queen of the Night	17.7	155	Smit, 2010
Safety Stove	23.2	216	Smit, 2010

Commercial ethanol-gel should meet the SABS standard for ethanol-gel, as specified in SANS 448. These requirements are shown in Table 8.

Table 8: SABS standards for ethanol-gel (SANS, 2010)

Property	**Requirements**
Viscosity at 25°C	> 25,000 cP
Flash point	> 23°C
Time taken to heat 1L of water from 25°C to 90°C	< 15 min
Residue (m/m)	< 5%

The ethanol-gel should further ignite readily and burn steadily, without flaring, sudden deflagrations, sparking, splitting, popping, dripping or exploding from ignition until it has burned to extinction (SANS, 2010).

CHAPTER 3

3. ETHANOL-GEL PRODUCTION AND WATER EXTRACTION

3.1 Introduction

In Chapter 3 the characterisation of the water hyacinth feedstock, as well as the experiments related to the production of ethanol-gel and the extraction of water from the water hyacinths, are discussed. The feedstock that was used in all the experiments of this study is described in Section 3.2, while the chemicals and enzymes used specifically for the production of the ethanol-gel and in the chemical extraction of water from the water hyacinths are described in Section 3.3. The production and testing of the ethanol-gel are discussed in Section 3.4. The experimental procedure followed in the chemical extraction of water, as well as the results of the water extraction, is discussed in Section 3.5. Concluding remarks are made in Section 3.6.

3.2 Feedstock

Water hyacinth (*Eichornia crassipes*) was harvested from the Vaal River near Parys (26°54'S 27°27'E) in the northwest region of the Free State province, South Africa. The water hyacinth feedstock was transported to the laboratory in air-tight containers to prevent the samples from losing water. In the laboratory of the North-West University the roots were separated from the leaves and the stems, in order to enable separate testing of the two parts of the water hyacinth as feedstock for bioenergy production. Characterisation of the feedstock was done by the Irene laboratories of the Agricultural Research Council (ARC) and the composition is shown in Table 9.

Table 9: Composition of roots, stems and leaves

Constituent	**Analyses**	**Stems and leaves (wt%, wet basis)**	**Roots (wt%, wet basis)**
Ash	ASM 048	2.10	2.63
Moisture content	ASM 013	84.44	90.56
Protein	Not SANAS accredited	1.89	0.21
Fat	ASM 044	0.21	0.08
Neutral detergent fibre (NDF)	ASM 060	7.88	3.73
Acid detergent fibre (ADF)	Not SANAS accredited	3.41	1.39
Acid detergent lignin (ADL)	Not SANAS accredited	0.32	0.62
Carbohydrates	ASM 075	9.68	5.57
Carbon to oxygen ratio	Elemental analysis	1.06	0.78

The moisture content of the water hyacinth pulp was also determined in-house by drying 100 g of wet water hyacinth pulp in an oven (Carbolite Laboratory Oven with natural convection) for 24 hours at 105°C. The dried water hyacinth, as shown in Figure 2, was weighed to calculate the moisture content, which was found to be 93.24 ± 0.75 wt%. This value compares well with the moisture content values obtained from the ARC, as well as values reported in literature (Nigam, 2002).

Figure 2: Dried water hyacinth leaves

From the ARC analysis the composition of the water hyacinth with regards to cellulose and hemicellulose could be calculated using the following equations (De Leon *et al.*, 2009):

$$\text{Cellulose} = (\text{ADF} - \text{ADL}) / (100\text{ wt\%} - \text{water content, wt\%}) \times 100 \quad (3.1)$$

$$\text{Hemicellulose} = (\text{NDF} - \text{ADF}) / (100\text{ wt\%} - \text{water content, wt\%}) \times 100 \quad (3.2)$$

The calculated results are compared to values from literature and shown in Table 10. The stems and leaves seem to be a more suitable feedstock than the roots, considering the higher cellulose and hemicellulose content, and a very low lignin content. The composition of the stems and leaves also compare well with the compositions found in literature. The roots, on the other hand, have a very low cellulose and crude protein content.

Table 10: Comparison of cellulose, hemicellulose, lignin and crude protein (dry basis wt%)

Constituent	**Stems and leaves**	**Roots**	**Comparative literature**			
			Lowest value	**Source**	**Highest value**	**Source**
Cellulose	19.9	8.2	17.8	Desai *et al.* (1993)	28.9	Luo *et al.* (2011)
Hemicellulose	28.7	24.8	18.4	Banerjee *et al.* (1991)	48.7	Nigam (2002)
Lignin	2.1	6.6	2.8	Ma *et al.* (2010)	27.7	Danon *et al.* (2008)
Crude protein	12.1	2.2	9.0	Murugesan & Radhika (2012)	21.0	Cen, *et al.* (2010)

The high cellulose content of the water hyacinth makes it ideal for the production of ethanol-gel, which comprises of alkali cellulose and ethanol. The production of bio-ethanol could also be feasible due to the presence of both cellulose and hemicellulose. As the water hyacinth contains a very high amount of water, it is paramount to extract the water prior to any further processing. As South Africa is a water scarce country, the suitability of the resulting extracted water should be considered for domestic, agricultural or industrial application. Thermochemical liquefaction is another possible production route to be followed with the added benefit that this process does not require extensive water removal, as water is a reagent during the process.

3.3 Chemicals

All the chemicals and enzymes used in the production of ethanol-gel, as well as in the extraction of water from the water hyacinths, are shown in Table 11. The purpose of these chemicals and enzymes, which were used as provided by the supplier without any further purification, is clearly indicated.

Table 11: Chemicals used in water extraction experiments

Component	**Details of components**	**Supplier**	**Purpose**
Water	Reverse osmosis, UV treatment and deionisation (Labostar TWF7 UV/DI)	Laboratory	Ethanol-gel production
Ethanol	99.95% pure	Rochelle chemicals	Ethanol-gel production
Sodium hypochlorite	2.5 vol% pure	Commercially available as JIK®	Bleaching agent
Nitric acid	70% pure	ACE	Acid pretreatment
Celluclast 1.5 L	15 wt% glucose content. Optimum pH of 4.5 – 6.0. Optimum temperature of 50 – 60°C.	Novozymes	Enzyme used during chemical water extraction
Pectinex ultra SP-L	5 wt% polygalacturonase content. Optimum pH of 4.5. Optimum temperature of 50°C.	Novozymes	Enzyme used during chemical water extraction
Tween 80	Saponification number of 45 – 55 mg KOH/g; hydroxyl number of 65 – 80 mg/g	Merck	Surfactant used during chemical water extraction
NaOH	98% pure	Labchem	pH adjustment during chemical water extraction
H_2SO_4	98% pure	Labchem	pH adjustment during chemical water extraction

3.4 Ethanol gel production

The experimental procedure consisted of the production of the ethanol-gel and the subsequent testing of the ethanol-gel, while the extraction of water from the water hyacinth entailed the chemical and enzymatic extraction of the water and the testing of the extracted water.

3.4.1 Experimental procedure

The overall experimental procedure is shown as a flow diagram in Figure 3.

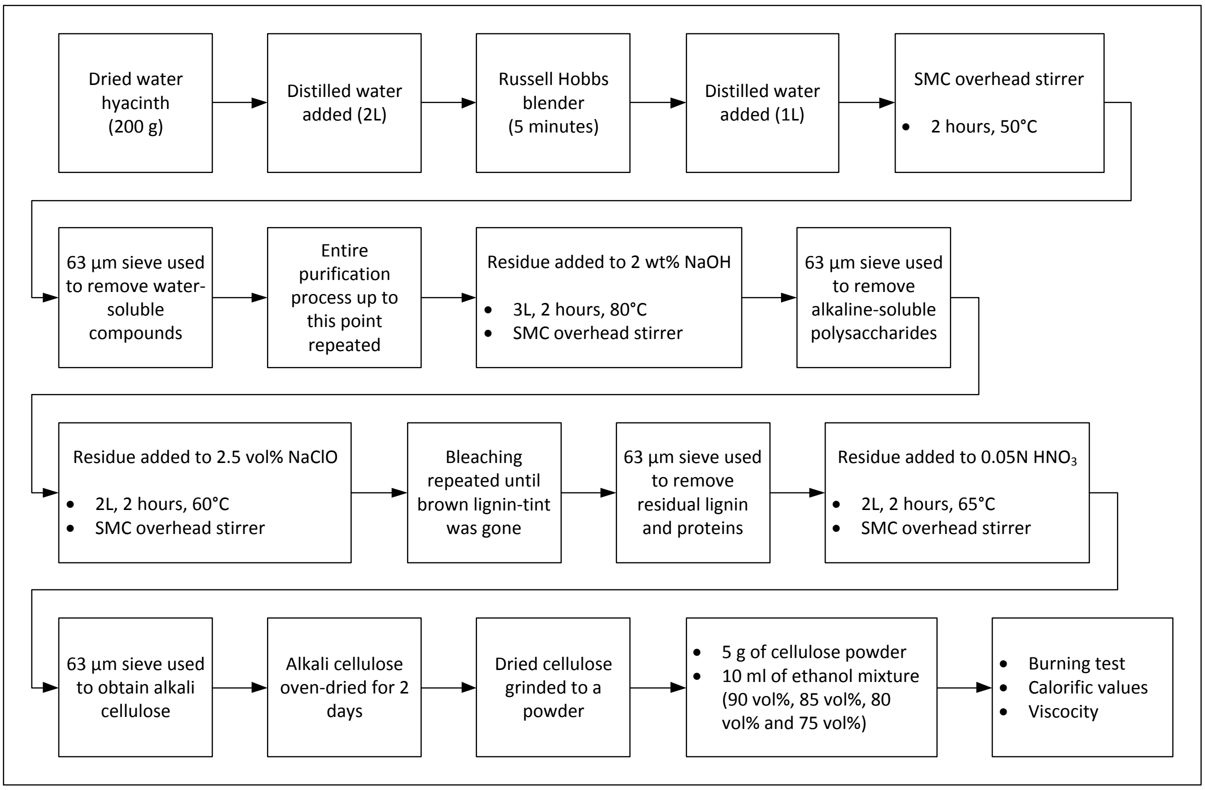

Figure 3: Experimental flow diagram for ethanol-gel production

The water hyacinth pulp was firstly dried to a final moisture content of 10 wt% for 3 days in an oven at 60°C, as shown in Figure 4. In order to break the fibres, the dried feedstock was ground to a particle size of ±1.5 mm.

Figure 4: Drying of water hyacinth in oven

In order to remove any water-soluble components, 100g of the dried, ground biomass was weighed off and added to 2L distilled water. The mixture was blended for 5 minutes in a Russell Hobbs blender at a blending speed of 10,000 rpm. The content was transferred to a 4000 ml Pyrex glass container and 1L of distilled water was added to the mixture. The mixture was stirred for 2h with a SMC overhead stirrer while the temperature was kept constant at 50°C using a water bath. A 63µm sieve was used to remove the water insoluble solids from the water soluble filtrate. This procedure was repeated twice.

The solid residue left after removal of water soluble components was treated with 3L of 2 wt% sodium hydroxide (NaOH) in a 4000 ml Pyrex glass container, placed in a water bath to maintain a temperature of 80°C for 2h, while stirring the mixture with a SMC overhead stirrer (see Figure 5) to remove polysaccharides and other inorganic material present. The solid residue left after the sodium hydroxide treatment was sieved using a 63µm sieve and washed with water to remove the polysaccharides and other inorganic material, while the insoluble cellulose remained in the residue.

Figure 5: NaOH pretreatment of purified water hyacinth mixture

The residue was then added to 2L of 2.5 vol% sodium hypochlorite (NaOCl) in a 4000 ml Pyrex glass container. The mixture was stirred for 2h at 60˚C (see Figure 6). The sodium hypochlorite served as bleaching agent, as well as to remove the residual lignin in the solid residue that added the brownish tint into the mixture. The mixture was again sieved using a 63µm sieve and the solid residue washed with water to remove any residual lignin and proteins.

Figure 6: Sodium hypochlorite treatment of water hyacinth solids

The solid residue left after leaching and removal of lignin was then added to 2L of 0.05N nitric acid in a 4000ml Pyrex glass container and stirred at 65˚C for 2h to remove acid soluble cellulose from the solids. The mixture was sieved through a 63μm sieve and thoroughly washed with water. The residue of this step was alkali cellulose, which was dried in the oven for 2 days.

The dried cellulose was ground to a fine powder using a coffee grinder and mixed with different ratios of water and alcohol to form an ethanol-gel, as shown in Figure 7. In each case 5 g of dry cellulose powder was mixed with 10 ml of liquid containing 90 vol%, 85 vol%, 80 vol% and 75 vol% ethanol respectively. The ethanol gave the gel the needed flammability. All tests stated below were performed on the 5 differently formulated ethanol-gels, as well as on a commercially available ethanol-gel, Liberty cooking gel.

Figure 7: Ethanol-gel from alkali cellulose extracted from water hyacinth

Ethanol-gel was successfully produced using cellulose extracted from the water hyacinth. The ethanol-gel was tested by determining the burning time, burning residue, higher heating value and viscosity. These results were compared to the SANS 448 standard for ethanol-gel, as well as to the results obtained from commercial ethanol-gel, Liberty cooking gel. These results are presented in Sections 3.4.2 to 3.4.5.

3.4.2 Burning test and waste residue

The ethanol-gels were burned in an hour glass and the burning time recorded using a stopwatch. The burning time was defined as the time from ignition until the flame was completely quenched. The residue after combustion was weighed and taken as the waste measurement. As specified in SANS 448 the residue of the ethanol-gel should not exceed 5 wt% of the initial ethanol-gel that was burnt. The average burning time of the different ethanol-gel ratios are shown in Figure 8.

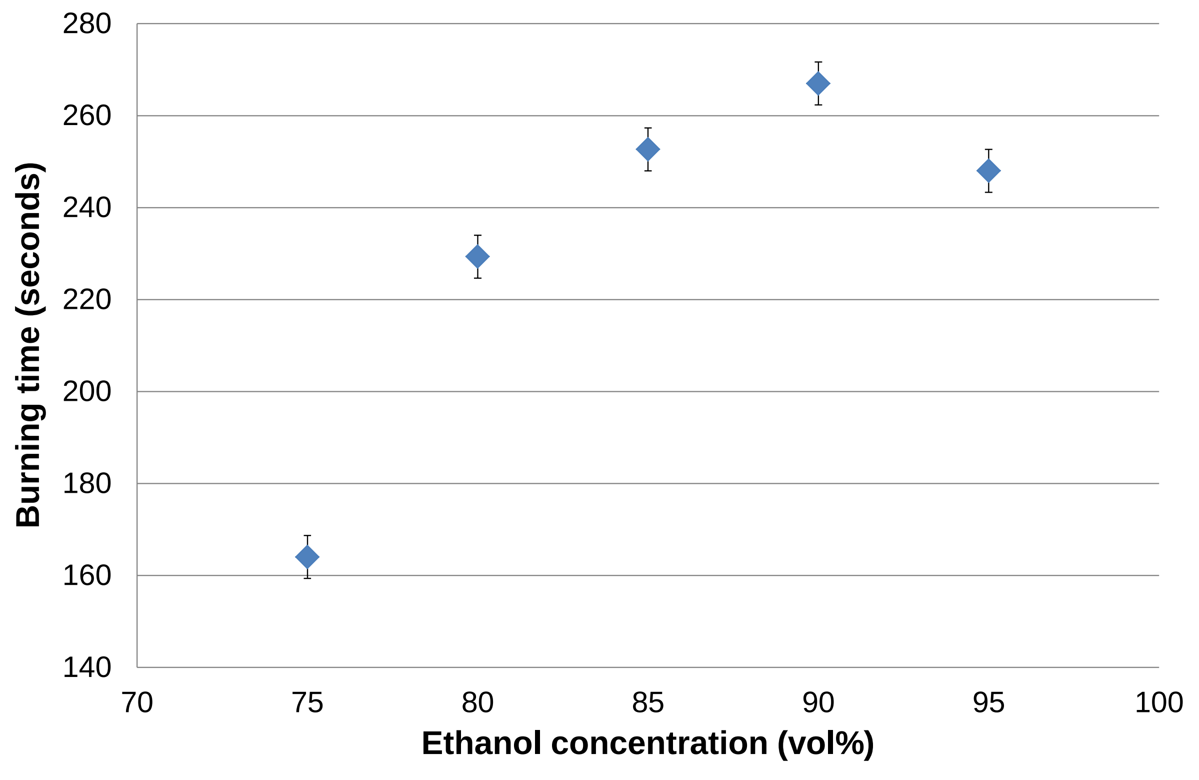

Figure 8: Burning time of ethanol-gel with different ethanol volume ratios

A maximum burning time of 267 ± 5 seconds was achieved using an ethanol-gel with a 90 vol% ethanol content. The burning time of the ethanol-gel increased with an increase in ethanol concentration up to the maximum burning point at 90 vol% ethanol content. Both the prepared ethanol-gel and the commercial Liberty cooking gel burned with a normal blue-orange flame. The average burning time for commercial Liberty cooking gel was 329 seconds, which is almost a minute longer than the prepared ethanol-gel. The waste residue of the ethanol-gel after each burn was measured and the results are presented in Figure 9.

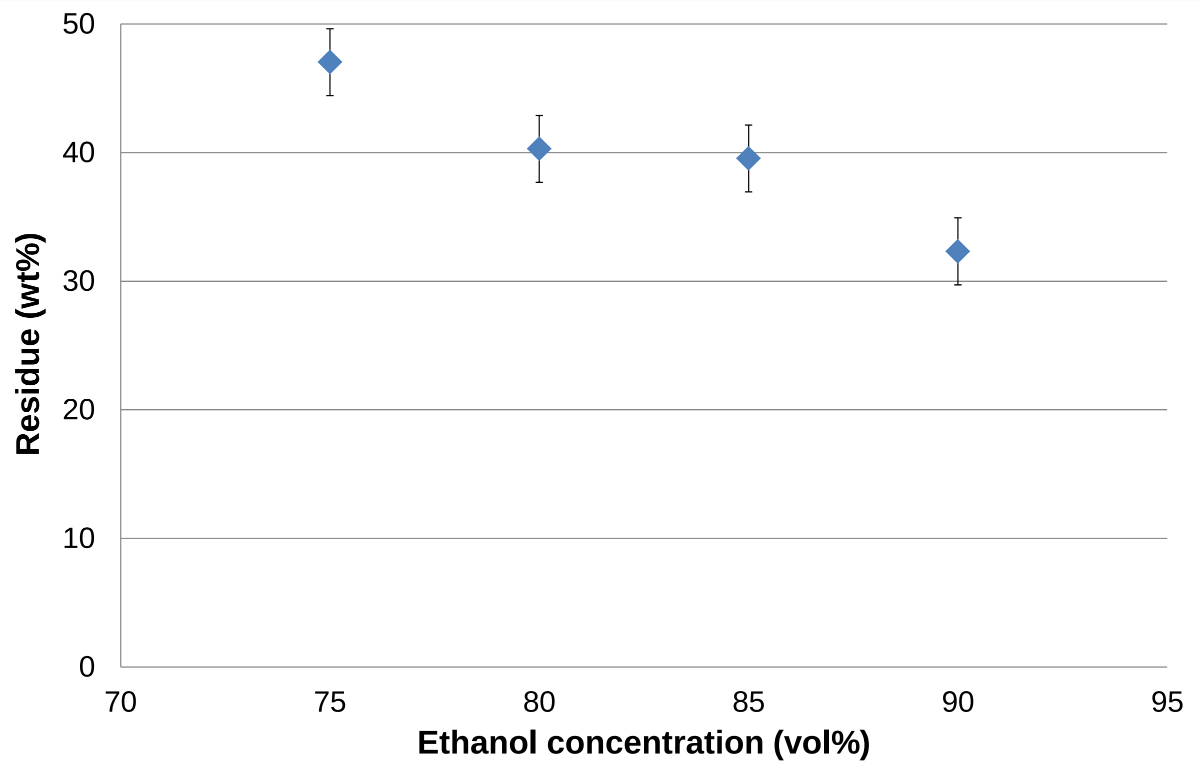

Figure 9: Residue after burning the ethanol-gel

As the ethanol concentration in the ethanol-gel is increased, there is a decreasing trend with regards to the amount of residue left after burning. As lower ethanol concentrations are associated with shorter burning times, the higher residues can be explained by incomplete combustion of all the material. The lowest residue of 32.3 ± 2.6 wt%, defined as the percentage of the mass of the ethanol-gel remaining after burning relative to the original ethanol-gel mass, was found with an ethanol-gel containing 90 vol% ethanol.

The average waste residue that remained after 5g of Liberty cooking gel was burned was 1.8 wt%. The commercial gel has a significantly lower amount of residue after burning, which can be explained by the fact that Liberty cooking gel was not produced from the cellulose of water hyacinth, but from refined cellulose from sawdust, waste paper and grass.

3.4.3 Higher heating values

The higher heating values of each sample were measured with an IKA C5003 Bomb-calorimeter. This was in accordance with SANS 1928, as specified in SANS 448. Each experiment required ± 1 g of gel sample. The ethanol-gel higher heating values (HHV) for the various ethanol concentrations are shown in Figure 10.

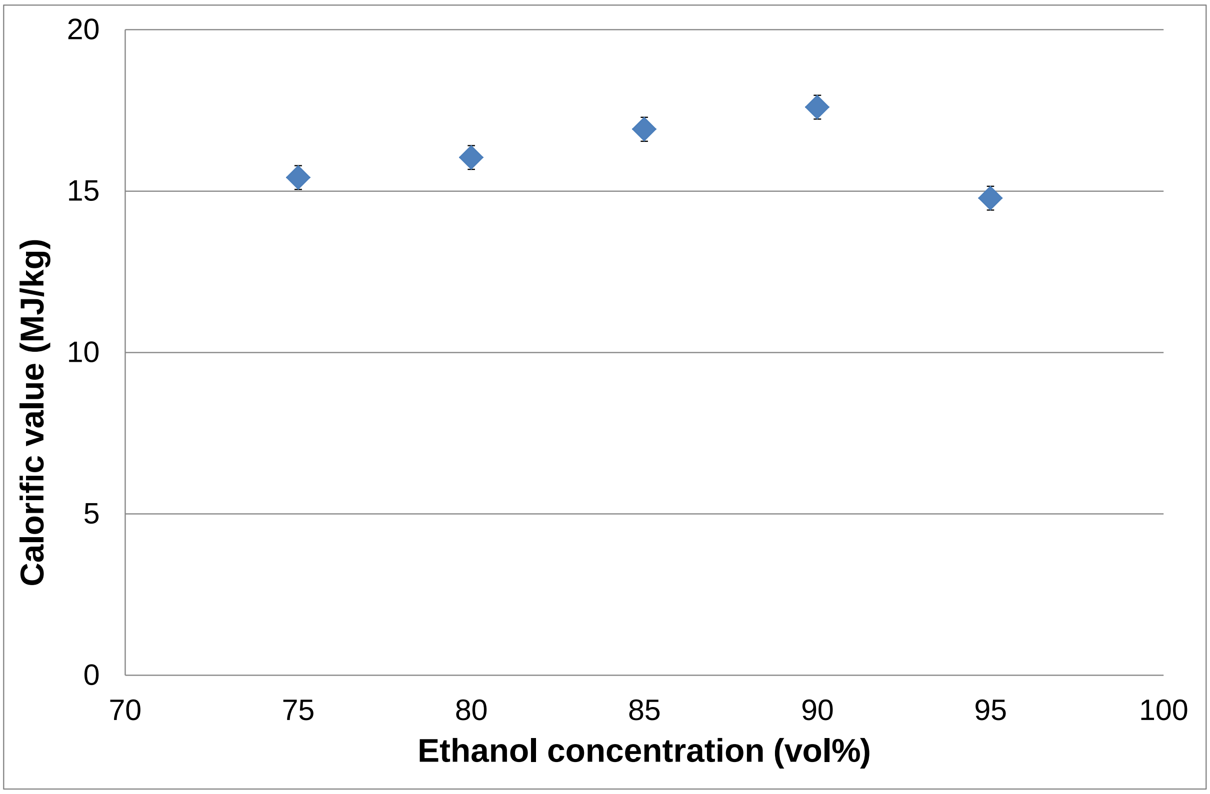

Figure 10: Higher heating values for ethanol-gel

An maximum higher heating value of 17.6 MJ/kg is achieved with the 90 vol% ethanol-gel. This is comparable to the higher heating value of 17.8 MJ/kg for Liberty cooking gel, as well as higher heating values of commercial gel fuels reported in literature (Lloyd & Visagie, 2007), shown in Table 12.

Table 12: Higher heating value of commercial gel fuels

Commercial gel fuel	**Higher heating value (MJ/kg)**
Sun gel	18.7
Enviro-Heat	18.6
Bio-Heat gel	17.7

3.4.4 Viscosity tests

The viscosities of the various ethanol-gels were determined by placing the R7 spindle of the Thermo-scientific viscometer in 50 ml of ethanol-gel. The spindle rotation speed was set to 0.5 rpm. The viscosities of the samples were measured at room temperature. This test was done in accordance with ISO 3104.

The viscosities of the ethanol-gels remain constant over the entire blending range. This can be explained by the fact that the volume of the water-ethanol mixture was not changed and furthermore that the viscosity of the water-ethanol mixture decreases by less than 3% as the ethanol concentration increases. The average viscosity was calculated to be 23,548 ± 1491 cP, which is slightly lower than the SANS 448 minimum requirement of 25,000 cP, as can be seen in Figure 11. The average viscosity of the Liberty cooking gel was 24,825 cP.

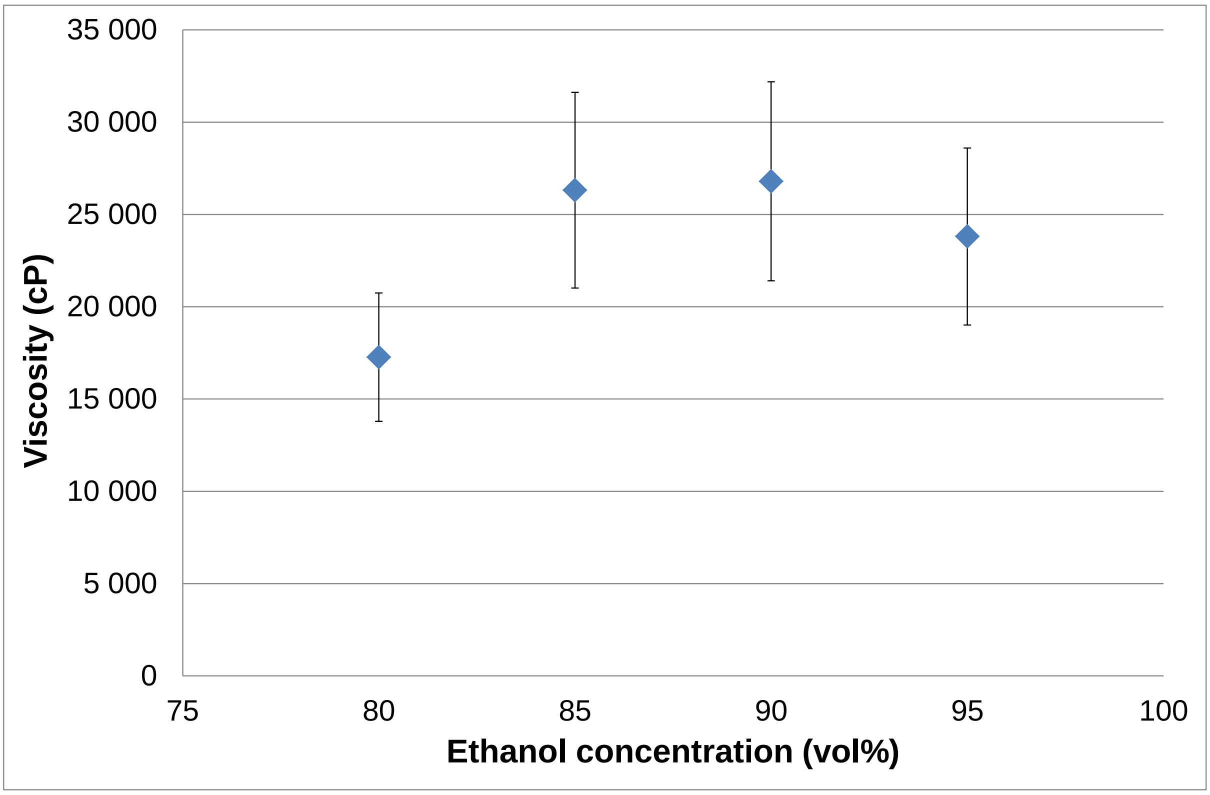

Figure 11: Effect of ethanol concentration on the viscosity of ethanol-gel

3.4.5 Product feasibility

The optimum ethanol-gel was produced using a 90 vol% ethanol ratio. In order to produce 1 L of 90 vol% ethanol-gel 16.4 kWh of energy was required. Using the current energy price of 80 c/kWh, the total energy cost involved to produce 1 L of ethanol-gel was R13 (Eskom, 2013). Another cost component was the chemicals used during the production. The total cost of chemicals to produce 1 L of ethanol-gel was calculated at R124, bringing the total cost to approximately R137, which is quite expensive if compared to the cost of Liberty cooking gel, which is available at a cost of R14 per litre on the market.

3.5 Recovery of water from water hyacinth

3.5.1 Experimental procedure

The water recovery experiments were conducted using only the leaves and stems of the water hyacinth. The stems and leaves were juiced with a Russell Hobbs blender to form a pulp medium (Figure 12).

Figure 12: Blending of water hyacinth

The pulp medium provided a high contact area for the added extraction agents (enzymes and surfactant). The pulverisation of the water hyacinth also assisted in the extraction of polysaccharides, including pectin and cellulose (Dufey *et al*., 2010). Two enzyme mixtures containing cellulase enzymes (Celluclast 1.5 L) and pectinase enzymes (Pectinex Ultra SP-L), as well as a surfactant (Tween 80), were used to chemically extract water from the water hyacinth pulp. First of all the separate effect of each extraction agent was considered, after which the combined effect of the cellulase and pectinase enzymes was evaluated. The experimental method for each extraction agent, as well as for the combined enzyme mixture, was identical. A 1000 ml Duran flask was filled with 100 g of water hyacinth pulp. A constant extraction agent dosage of 0.07 g (0.07 wt%) was added to the pulp in the case of the enzyme mixture, (Celluclast 1.5 L and Pectinex Ultra SP-L), while a dosage of 0.125 g (0.125 wt%) was used in the case of the surfactant (Tween 80). Similar dosages were used for the combined experiments.

The influence of temperature and pH on the amount of water extracted from stems and leaves of water hyacinth was investigated. All experiments were done in a standard incubation oven (Scientific Series 2000) to ensure constant temperature for the duration of each experiment. The influence of the pH of the pulp was investigated by varying the pH between 2.5 and 6.5 through the addition of either NaOH or sulphuric acid (H_2SO_4) at a constant temperature of 40°C. The influence of temperature on the amount of water extracted was investigated by varying the temperature between 30°C and 50°C at a constant pH of 4.5. The treatment time for all experiments was kept constant at one hour (Bothma *et al.*, 2013).

Upon completion of the extraction experiment the temperature in the oven was increased to 99°C for 20 minutes to allow for the denaturation of the enzymes. After cooling, a Büchner filter was used to separate the solids from the extracted water. The yield was determined by weighing the mass of the water obtained after filtration. A flow diagram of the water extraction experiments is shown in Figure 13.

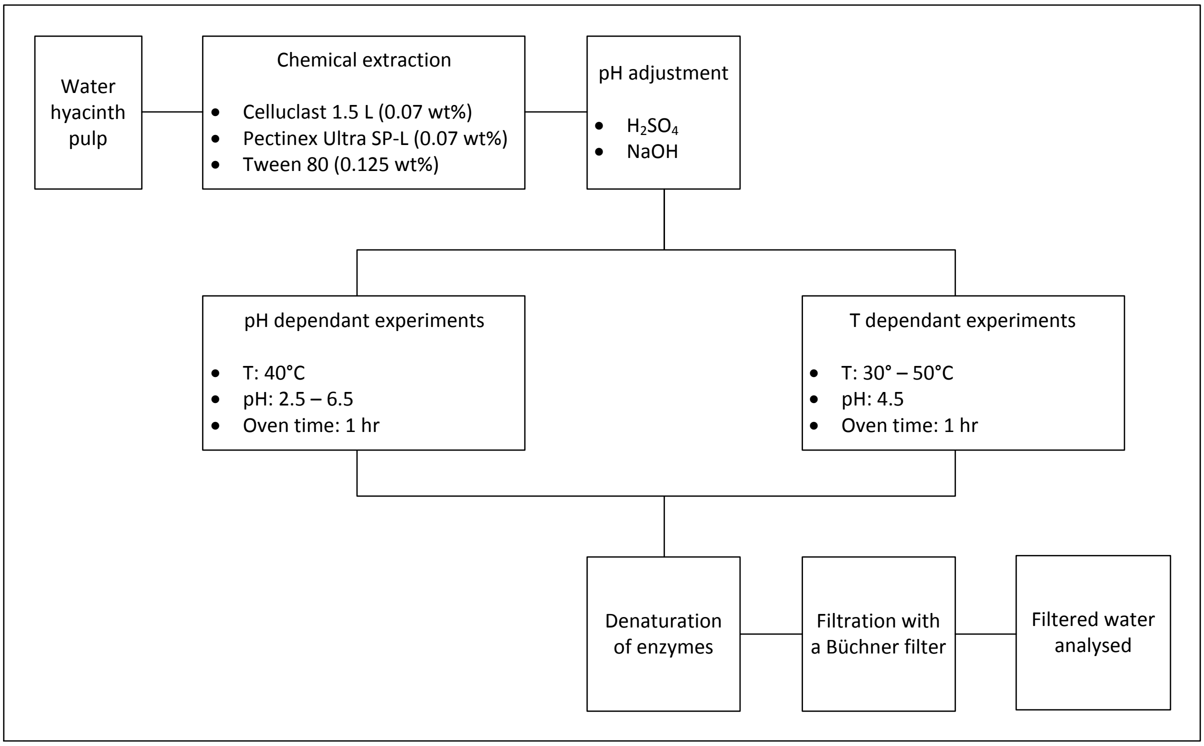

Figure 13: Flow diagram of water extraction experiments

High biomass loadings increase the viscosity of the mixture, thus making it more difficult for the enzymes to access the solids. The effect of lowering the viscosity of the mixture, and subsequently increasing the accessibility of the solids, was investigated by dilution of the mixture with 140 ml either purified water or extracted water to ensure that the pulp was totally submerged in the water.

The extracted water was further purified using activated carbon and a sediment filter. The purpose of the additional purification was to assess the difference in water quality of the filtered and unfiltered water. All water samples were analysed before and after purification.

A complete elemental analysis was done by the Envirocare Laboratory in Potchefstroom on the extracted water in order to determine the water quality. The total dissolved solids (TDS) were measured with a Hanna TDS Tester.

3.5.2 Influence of pH on water yield

The influence of pH on the amount of water extracted was investigated by varying the pH from 2.5 to 6.5 at a constant temperature of 40°C and a treatment time of 1 hr. The experimental error associated with this set of experiments was calculated to be 0.05 $g_{water}/g_{water\ in\ biomass}$ at a 95% confidence level and is indicated with error bars in Figure 14.

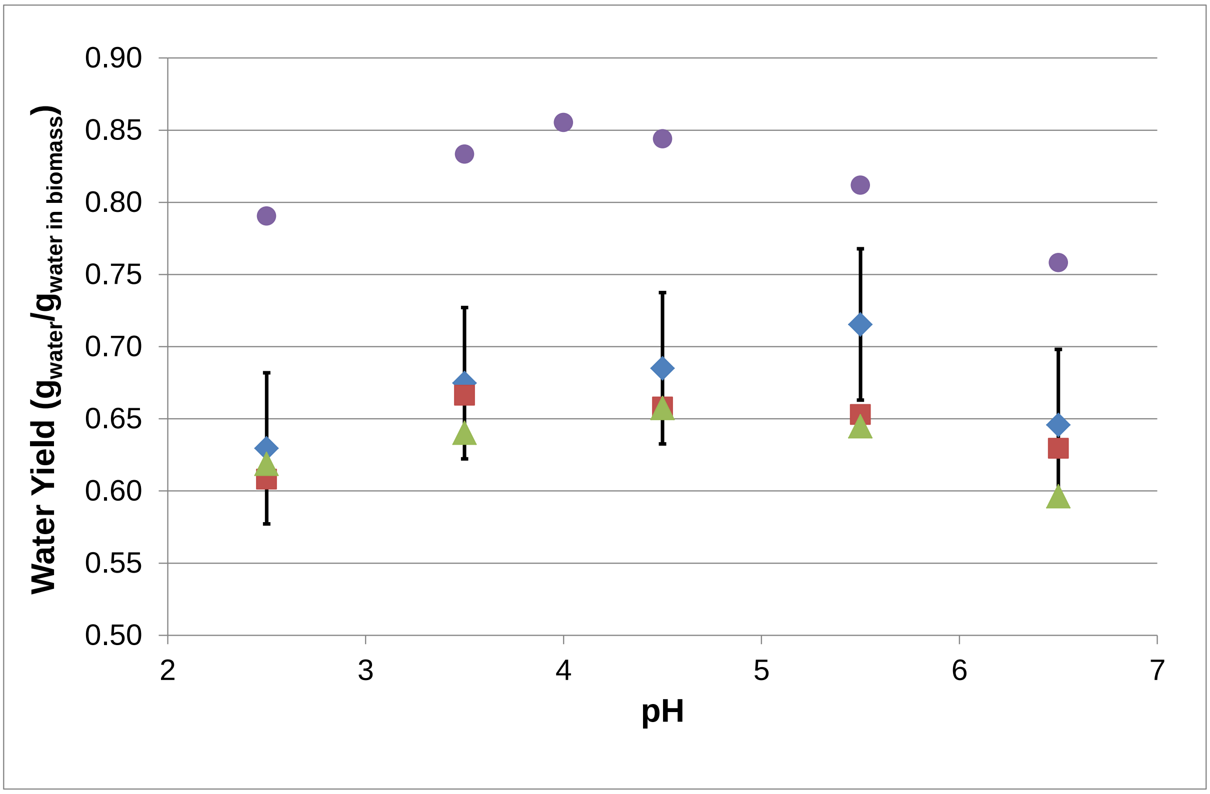

Figure 14: Influence of pH on water yield (◆ Celluclast 1.5 L, ■ Pectinex Ultra SP-L, ▲ Tween 80, ● combination of Celluclast 1.5 L and Pectinex Ultra SP-L)

There is an increase in water yield with an increase in pH for all treatment agents and combination up to a maximum, followed by a decrease in water yield with a further increase in pH. This observation corresponds to the active pH range of the enzyme mixtures used (Kargi & Shuler, 2008).

The pH that corresponded to the maximum amount of water extracted was found to be 5.5, 3.5 and 4.5 for Celluclast 1.5 L, Pectinex Ultra SP-L and Tween 80 respectively. These pH levels correspond to the optimum pH specified by the enzyme suppliers. The highest water yield obtained for Celluclast 1.5 L, Pectinex Ultra SP-L and Tween 80 was 0.72 ± 0.05 $g_{water}/g_{water\ in\ biomass}$, 0.67 ± 0.05 $g_{water}/g_{water\ in\ biomass}$ and 0.66 ± 0.05 $g_{water}/g_{water\ in\ biomass}$ respectively. Due to the high experimental error, the average yield for all the different treatments using only one extraction agent is approximately the same.

There is, however, a clear benefit in using a combination of Celluclast 1.5 L and Pectinex Ultra SP-L with a significant increase in water yield up to 0.86 ± 0.05 $g_{water}/g_{water\ in\ biomass}$ at a pH 4. The reason for this higher yield is directly related to the synergistic working of the added enzymes. Celluclast 1.5 L contains mostly cellulose enzymes and assists in the breakdown of cellulosic materials, while Pectinex Ultra SP-L breaks down the pectin in the cell walls of the water hyacinth [National centre for biotechnology education, 2012a]. Pectinex Ultra SP-L, which is a mixture of enzymes, also contains small amounts of hemicellulase and cellulase [National centre for biotechnology education, 2012b].

3.5.3 Influence of temperature on water yield

The effect of temperature on the water yield was investigated at a constant pH of 4.5 and treatment time of 1 hr with the temperature varied from 30°C to 50°C. The experimental error associated with the set of experiments was calculated to be 0.05 $g_{water}/g_{water\ in\ biomass}$ at a 95% confidence level and is indicated with error bars in Figure 15.

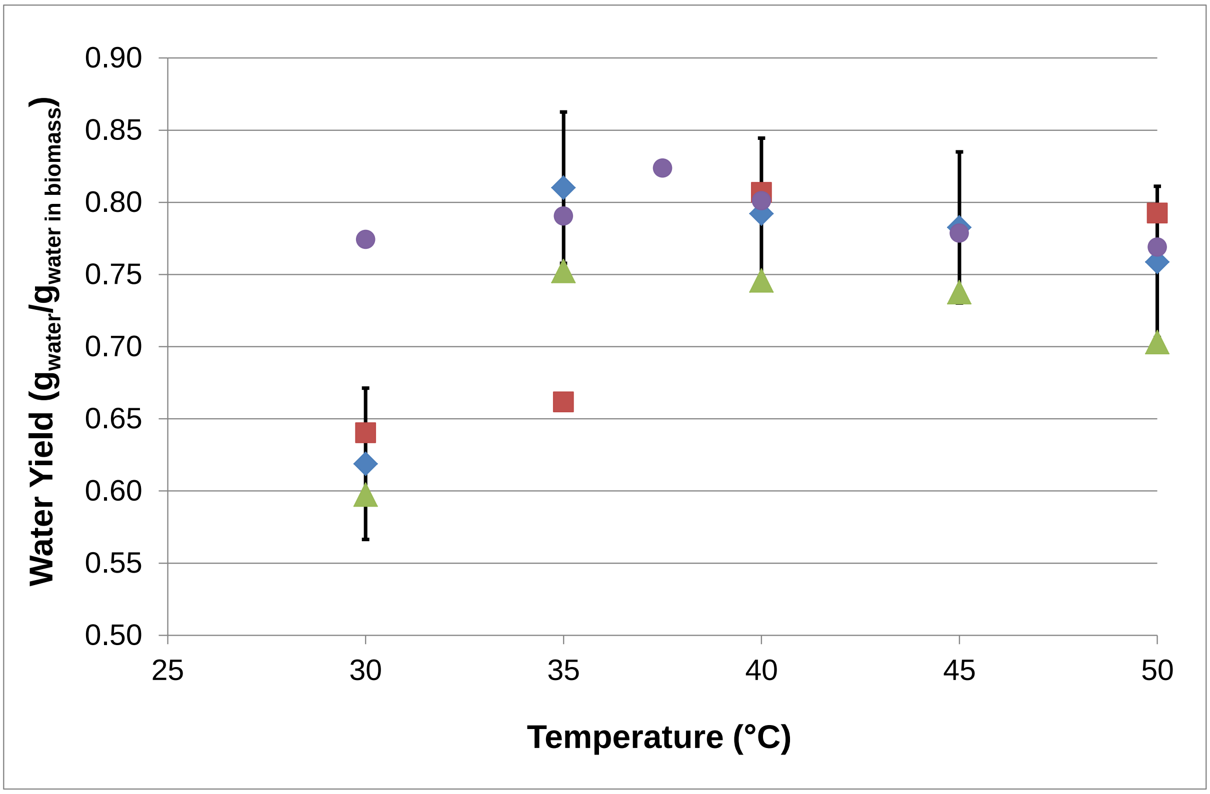

Figure 15: Influence of temperature on water yield (◆ Celluclast 1.5 L, ■ Pectinex Ultra SP-L, ▲ Tween 80, ● combination of Celluclast 1.5 L and Pectinex Ultra SP-L)

With an increase in temperature there is an initial increase in water yield, after which the water yield remains almost constant for all of the additives due to the large experimental error. It was expected that the water yield would increase with an increase in temperature as the rate of enzyme-catalysed reactions increases with an increase in temperature, up to a certain temperature, after which enzyme activity will decrease due to denaturation of the enzymes (Kargi & Shuler, 2008).

The temperature at which most water was extracted for both Celluclast 1.5 L (0.81 ± 0.05 $g_{water}/g_{water\ in\ biomass}$) and Tween 80 (0.75 ± 0.05 $g_{water}/g_{water\ in\ biomass}$) was found to be 35°C, which compares well with the optimum temperature of 40°C obtained in a similar study (Bothma *et al.*, 2013). The highest water yield (0.81 ± 0.05 $g_{water}/g_{water\ in\ biomass}$) with Pectinex Ultra SP–L as additive was obtained at a temperature of 40°C. Bothma *et al.* (2013) also found 40°C to be the optimum extraction temperature when using Pectinex Ultra SP-L.

There is a slight increase in water yield (0.82 $g_{water}/g_{water\ in\ biomass}$) in the case where both Celluclast 1.5 L and Pectinex Ultra SP-L were used, but this lies within the experimental error of the results obtained using only a single extraction agent.

3.5.4 Influence of addition of water to the extraction yield

It was considered whether the water extraction could not be further increased by the addition of supplementary de-ionised water, as well as recycled water. It was expected that the additional water would lower the viscosity and increase the accessibility of the enzymes. The effect of the addition of water (de-ionised and recycled) is summarised in Figure 16.

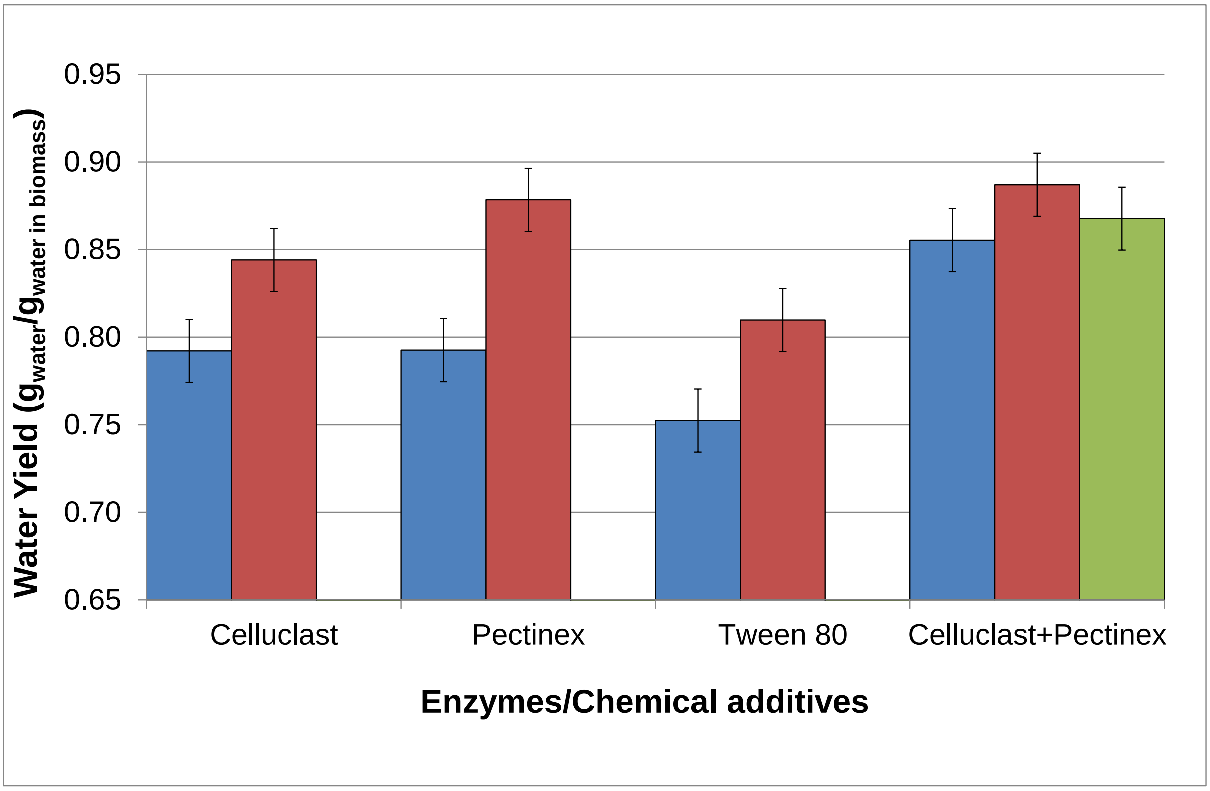

Figure 16: Summary of experiments conducted both with and without water (🟦 no additional water; 🟥 with additional de-ionised water; 🟩 with additional recycled extracted water)

The addition of supplementary water increased the average yield of extracted water with up to 0.09 $g_{water}/g_{water\ in\ biomass}$. The addition of water lowered the viscosity and increased the contact area of the additives with the water hyacinth pulp, resulting in an increase in the active area of the additives. The addition of water to the experiments containing the combination of Celluclast 1.5 L and Pectinex Ultra SP-L delivered the highest yield of 0.89 ± 0.01 $g_{water}/g_{water\ in\ biomass}$. Using recycled water instead of de-ionised water showed only a slightly lower yield of 0.87 ± 0.01 $g_{water}/g_{water\ in\ biomass}$, but it was still higher than the yield obtained when no additional water was added during the experiment.

In conclusion it can be stated that the worst extractive agent throughout all the water extraction experiments was Tween 80, with a maximum water extraction yield of 0.81 ± 0.01 $g_{water}/g_{water\ in\ biomass}$. This can be explained by the fact that Tween 80 is a detergent (soap) and belongs to a group of compounds known as surfactants (Da Silva *et al.*, 2007). Surfactants are surface active agents that reduce the interfacial surface tension in mixtures through adsorbing to the interfaces, but in the case of the water hyacinth would not have altered the physical structure of the pulp to increase the extraction of water from the cellulosic and pectinolytic structures present in the water hyacinth plants.

The highest yield throughout all the experiments was obtained using a combination of Celluclast 1.5 L and Pectinex Ultra SP-L and additional de-ionised water. A yield of 0.89 ± 0.01 $g_{water}/g_{water\ in\ biomass}$ was realised, followed by a yield of 0.88 ± 0.01 $g_{water}/g_{water\ in\ biomass}$ obtained using only Pectinex Ultra SP-L and de-ionised water. It is thus recommended to use only Pectinex Ultra SP-L and de-ionised water. A pH of 3.5 and a temperature of 40°C should be used as these are the optimum operating conditions found during this study. Using one enzyme instead of two reduces operating costs and simplifies the chemical extraction process.

3.5.5 Water quality

The quality of the water obtained via chemical extraction was determined in order to establish whether the water was suitable for domestic, industrial or agricultural application. Multiple factors, including the total dissolved solids (TDS) level, total hardness, sodium adsorption ratio (SAR), as well as the concentration of certain constituents, were considered.

3.5.5.1 TDS

The Department of Water Affairs (DWA), previously known as the Department of Water Affairs and Forestry (DWAF), defines total dissolved solids (TDS) as a measure of the amount of inorganic salts dissolved in water (Department of Water Affairs, 1996a). The average TDS value calculated for the unfiltered water yielded at optimal process conditions were approximately 8940 ± 79.5 mg/L. According to the Department of Water Affairs, the target TDS levels range from 0 to 100 mg/L and 0 to 450 mg/L for industrial and domestic water respectively. The maximum TDS level in water used for irrigation is 260 mg/L. The measured TDS level is thus well above the target ranges provided and thus not suitable in its unfiltered state for domestic, industrial or agricultural purposes (Department of Water Affairs, 1996b).

Filtration with sediment and activated carbon filters will not effectively reduce the TDS levels. Sediment filters remove suspended matter such as sand, slit and organic material from water, while activated carbon filters reduce the amount of ions and metals such as chlorine and radon (Dvorak & Skipton, 2008a). These filters are known as pre-filters due to the fact that they are implemented prior to a reverse osmosis membrane in water treatment systems. A reverse osmosis system, on the other hand, reduces the TDS levels in the water, as well as the suspended particles within the water (Dvorak & Skipton, 2008b). In order to reduce the TDS levels below acceptable levels for domestic, industrial or agricultural use reverse osmosis would be required.

3.5.5.2 Metals

A full compositional analysis was performed on both the unfiltered extracted water and the filtered extracted water to determine which macro-elements are present. Sediment and carbon filters were used for the purpose of filtering. All elements present in quantities larger than 0.5 mg/L are presented in Table 13.

Table 13: Metals present in filtered and unfiltered extracted water

Element	Unfiltered sample (mg/L)	Filtered sample (mg/L)
K	372.9	91.3
Mg	25.6	0.6
Na	12.8	9.3
Ca	9.4	0.0015
Mn	7.7	0.11
Rb	3.1	0.69
Cu	1.0	0.043
Fe	0.6	0.01

The filtered sample shows lower quantities of all the notable metals present. The notable presence of manganese (Mn), rubidium (Rb), copper (Cu) and iron (Fe) in the water may be the result of gold mining and industrial activities in the Vaal Barrage area near Parys where the water hyacinths were harvested. The calcium (Ca) and magnesium (Mg) levels were used in the calculation of the total hardness, as well as the sodium adsorption ratio (SAR) of the extracted water.

3.5.5.3 Total hardness

The scale-forming and corrosive potential of water is directly related to the equilibrium saturation point of the water and thus hard water may have significant impacts on irrigation systems. Total hardness of water may be described as the combined concentrations of magnesium and calcium present in the water and is usually expressed as mg $CaCO_3$/L. The total hardness of water may be calculated with the following equation provided by the Department of Water Affairs (1996b):

$$\text{Total hardness (mg } CaCO_3\text{ /L)} = 2.497 \times [\text{mg Ca/L}] + 4.118 \times [\text{mg Mg/L}] \qquad (3.3)$$

Total hardness levels obtained from experiments conducted at optimal process conditions indicated the average level of unfiltered and filtered water is 130 ± 5.4 mg/L (slightly hard) and 2.5 ± 0.061 mg/L (soft) respectively. These levels comply with both industrial and domestic standards. There is, however, no standard available concerning agricultural application.

3.5.5.4 Sodium adsorption ratio (SAR)

Soil sodicity is the percentage of a soil's cation exchange capacity occupied by sodium ions. The sodium adsorption ratio (SAR) is an indication of the potential of particular irrigation water to induce sodic soil conditions. The SAR is calculated from the sodium, calcium and magnesium concentrations present in the water and provide an indication of the level where the exchangeable sodium percentage (ESP) of the soil will stabilize after extensive irrigation (Dvorak & Skipton, 2008a).

The SAR guidelines are only applicable to irrigation water, as this factor is only important from an agricultural point of view. The SAR of irrigation water is calculated with the following equation:

$$SAR = \frac{[sodium]}{\sqrt{0.5([calcium]+[magnesium])}} \tag{3.4}$$

with the sodium, calcium and magnesium concentrations present in the solution measured in mmol/L. With the optimal SAR ≤ 2.0, the SAR levels obtained for the unfiltered water satisfy the provided irrigation guidelines with an average value of approximately 0.36 ± 0.01.

3.5.5.5 Salinity

Salinity is a measure of the salt content (including sodium and potassium salts) of water or soil. Accumulation of such salts in the root area of plants may negatively impact the growth yield of horticultural crops. The average potassium concentrations obtained for the unfiltered and filtered experiments were 376 ± 9 mg/L and 96 ± 10 mg/L, which is well above the optimal salinity range for domestic water of 0 to 50 mg/L. No guidelines are provided for industrial and agricultural water. High potassium concentrations in water may result in the water having a noticeable bitter taste and cause electrolyte disturbances in sensitive individuals (Department of Water Affairs, 1996a).

The average sodium concentrations acquired for the unfiltered and filtered experiments were 12 ± 0.6 mg/L and 9 ± 0.4 mg/L respectively and within the domestic target range of 0 to 100 mg/L specified by Department of Water Affairs (1996a). Such low levels of sodium in the water have no aesthetic or health effects. With an agricultural sodium target range concentration of 0-70 mg/L, utilization of such water for irrigation should prevent the accumulation of sodium to toxic levels in most crops with the exception of extremely sensitive plants (Department of Water Affairs, 1996b).

3.5.5.6 Phosphates

The implementation of mineral phosphorus fertilizer enabled crop farmers around the world to replenish the phosphorus lost from the soil during the harvesting process of crops. Since the use of phosphorus in fertilizers, substantial increases in the agricultural yields have been observed. Food production has become extremely dependant on the use of phosphorus fertilizers (Department of Water Affairs, 1996b).

In order to be suitable for agricultural purposes the phosphate level should not exceed 5000 mg/L (Department of Water Affairs, 1996b). The average unfiltered water displayed an average phosphate concentration of 104 ± 6 mg/L, while the filtered water indicated an average of 23 ± 4 mg/L, making the water suitable for irrigation.

3.5.5.7 Manganese

Manganese is an essential plant nutrient and appears to be required as an enzyme activator. Manganese concentrations are highest in the reproductive sections (seeds) of the plants and lowest in the woody parts (Department of Water Affairs, 1996b). The respective average manganese concentrations obtained in the unfiltered and filtered water were 7.5 ± 0.6 mg/L and 0.11 ± 0.01 mg/L. Irrigation standards provided by the Department of Water Affairs (1996b) indicated that manganese concentrations in the range of 0.02 to 10.0 mg/L is the maximum allowable concentrations for fine-textured neutral to alkaline soils, but the target range is 0-0.02 mg/L. Thus both unfiltered and filtered water are above the target range.

The target range relating to industrial use is between 0 and 0.05 mg/L (Department of Water Affairs, 1996c). Manganese concentrations present in the unfiltered water are well above the target levels and may cause damage due to precipitation of manganese compounds. Filtered water, on the other hand, showed levels much lower, but still higher than the target of 0.05 mg/L, having thus the potential of causing moderate damage as a result of precipitation.

Standards regarding domestic use require a target range of 0 to 0.05 mg/L. Unfiltered water may have severe aesthetical effects, although health effects are rare. Filtered water is in the threshold for significant staining and taste problems (Department of Water Affairs, 1996a).

3.6 Concluding remarks

Ethanol-gel produced from alkaline cellulose extracted from water hyacinth and containing 90 vol% ethanol and 10 vol% water was compared to the SANS 448 standard for ethanol-gel (SANS, 2010), as shown in Table 14.

Table 14: A comparison of the ethanol-gel with the SABS standards for ethanol-gel

Property	Value	Requirements
Viscosity at 25°C	23,548 cP	> 25,000 cP
Residue (m/m)	32 wt%	< 5%
Ethanol concentration	90 vol%	> 80 vol%

The viscosity and residue parameters of the produced gel fall outside of the requirements as specified by the SANS448 standard for ethanol gel. The ethanol-gel was found to ignite readily and burn steadily, without flaring, sudden deflagrations, sparking, splitting, popping, dripping or exploding from ignition until it had burned to extinction, as required by SANS 448 (SANS, 2010). The requirement with regards to the viscosity can be easily overcome by refining the production process, as the current viscosity lies within the experimental error of the required viscosity (23,548 ± 1491 cP).

The other major challenge, however, with producing ethanol-gel from water hyacinth is the high amount of residue remaining after burning. Even if this problem can be overcome, the fact remains that there are extremely high costs involved with the manufacturing of ethanol-gel from water hyacinth cellulose. For each gram of ethanol-gel that was produced, 0.4 g of wet water hyacinth was required. The drying and pretreatment of the water hyacinth, as well as the additional chemicals required in the production of the ethanol-gel, shows that ethanol-gel cannot be economically produced using water hyacinth as feedstock.

The applicability of the unfiltered en filtered water extracted from water hyacinth stems and leaves is summarised in Table 15.

Table 15: Applicability of unfiltered and filtered water (I-Industrial, D-Domestic, A-Agricultural)

Parameter	Unfiltered water	Applicability	Filtered water	Applicability
TDS (mg/L)	8940 ± 79.5	None	8940 ± 79.5	None
Total hardness (mg/L)	130 ± 5.44	I, D, A	2.4 ± 0.061	I, D, A
SAR	0.36 ± 0.01	I, D, A	Did not analyse	
Potassium	376 ± 9	I, A	96 ± 10	I, A
Sodium	12 ± 0.6	I, D, A	9 ± 0.4	I, D, A
Phosphates	104 ± 6	I, D, A	23 ± 4	I, D, A
Manganese	7.5 ± 0.6	I, A	0.11 ± 0.01	I, A

It can be concluded that the extracted water, both filtered and unfiltered, is not suitable for domestic use without further purification to reduce the TDS, potassium and manganese levels. The unfiltered and filtered water is, however, suitable for industrial and agricultural purposes, except when considering the TDS levels. As stated earlier, a reverse osmosis system would be required to reduce the TDS and suspended particle level to such an extent that the water would be suitable for domestic, industrial or agricultural use (Dvorak & Skipton, 2008b).

CHAPTER 4

4. ULTRASONIC PRETREATMENT

4.1 Introduction

The potential ethanol production from sugars derived from water hyacinth, using ultrasonic pretreatment, is discussed in this chapter. The feedstock is described in Section 4.2, while the chemicals used specifically for the ultrasonic pretreatment are discussed in Section 4.3. The experimental procedure for the pretreatment is provided in Section 4.4. The fermentable sugars obtained through ultrasonic pretreatment and theoretical obtainable ethanol yields are discussed in Section 4.5.

4.2 Feedstock

Only the water hyacinth roots were used for the ultrasonic pretreatment experiments. The roots were dried to a final moisture content of 10 wt%, after which the roots were milled to a particle size of ±1.5 mm. As shown in Table 10, it was calculated that the roots have a cellulose content of 8.2 wt% and a hemicellulose content of 24.8 wt% on a dry basis. The maximum theoretical sugar yield was calculated to be 0.33 g/g biomass.

4.3 Chemicals, microorganisms and media

All the chemicals used in the ultrasonic pretreatment experiments, as well as the purpose of these chemicals, are shown in Table 16. The chemicals were used as provided by the supplier without any further purification.

Table 16: Chemicals used in the pretreatment experiments

Component	**Details of components**	**Supplier**	**Purpose**
Arabinose	99% pure	Sigma-Aldrich	Used for arabinose calibration curve
Cellubiose	99% pure	Sigma-Aldrich	Used for cellubiose calibration curve
Ethanol	99% pure	Sigma-Aldrich	Used for ethanol calibration curve
Fructose	99% pure	Sigma-Aldrich	Used for fructose calibration curve
Galactose	99% pure	Sigma-Aldrich	Used for galactose calibration curve
Mannose	99% pure	Sigma-Aldrich	Used for mannose calibration curve
Sodium hydroxide	98% pure	Labchem	Base pretreatment and pH adjustment
Sucrose	99% pure	Sigma-Aldrich	Used for sucrose calibration curve

4.4 Experimental procedure

Ultrasonic pretreatment of water hyacinth biomass was done using both indirect (ELMA® ultrasonic bath) and direct (QSonica® ultrasonic probe) sonication. The experimental procedure is summarised in a flow diagram, shown in Figure 17.

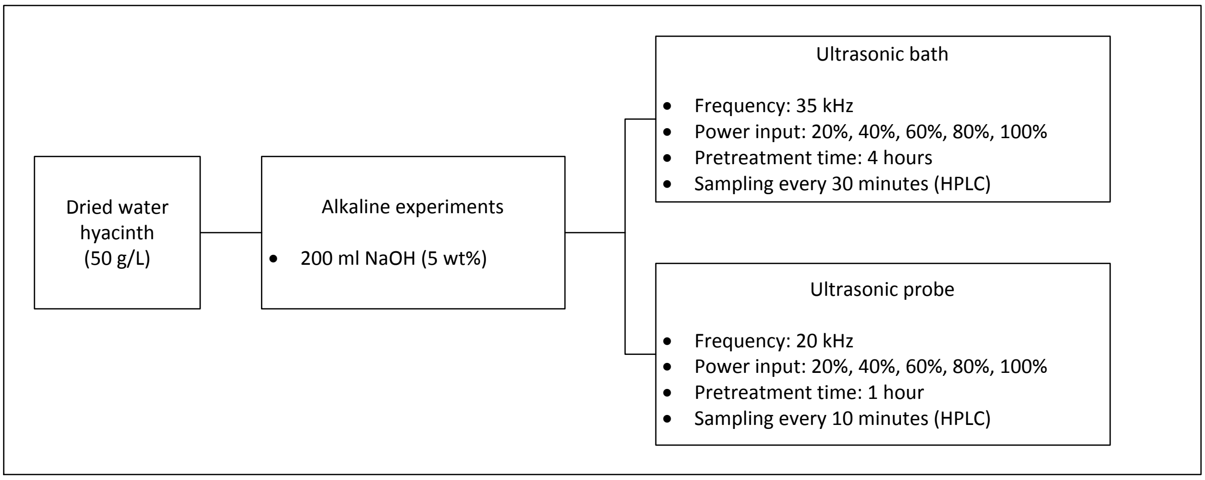

Figure 17: Flow diagram of ultrasonic pretreatment of water hyacinth roots

4.4.1 Indirect sonication

Indirect sonication experiments were done using an ELMA® ultrasonic bath. NaOH (200 mL, 5 wt%) was placed in 250 ml Scott Duran® bottles. Dried water hyacinth (10g, 50 g/L) was added to the alkaline solution and shaken to ensure the biomass was thoroughly distributed in the solution. The bottles were then placed inside the water-filled ultrasonic bath.

A frequency of 35 kHz was used, as a previous study proved that higher frequencies do not lead to higher sugar yields (Brandling *et al.*, 2011). The ultrasonic bath allows three modes of operation namely sweep, degas and normal, of which only normal was tested. The power setting of the ultrasonic bath was varied from 150 W to 750 W, using 150 W increments. The total pretreatment time was 4 hours, taking 2 ml samples every 30 minutes using a pipette. These samples were filtered using a 0.45 micron filter and diluted using 0.2 µl of the sample, 0.2 µl 2-butanol stock solution (internal standard) and 5 ml water. The pH of the samples was adjusted to 7 and further filtered using a 0.2 micron filter. An Agilent 1200 high-performance liquid chromatography (HPLC) system was used for all analyses.

4.4.2 *Direct sonication*

Direct sonication experiments were done using a QSonica® ultrasonic probe. The ultrasonic probe is lowered into a 250 ml Scott Duran® bottle filled with 200 ml NaOH (5 wt%) and 10 g of dried water hyacinth (50 g/L). The sampling was done every 10 minutes, resulting in a total of 6 samples being taken during the entire pretreatment period. The direct probe was operated with a frequency of 20 kHz and a power input of 700 W. An Agilent 1200 high-performance liquid chromatography (HPLC) system was used for all analyses.

4.5 Results

4.5.1 *Pretreatment using indirect sonication*

The first parameter of importance during sonication is the energy input, as shown in Figure 18. Higher sugar yields were obtained at the lowest energy input. The decrease in sugar yield can be explained by the degradation in sugars during pretreatment with a higher energy input, as was also found by Abidin *et al.* (2011).

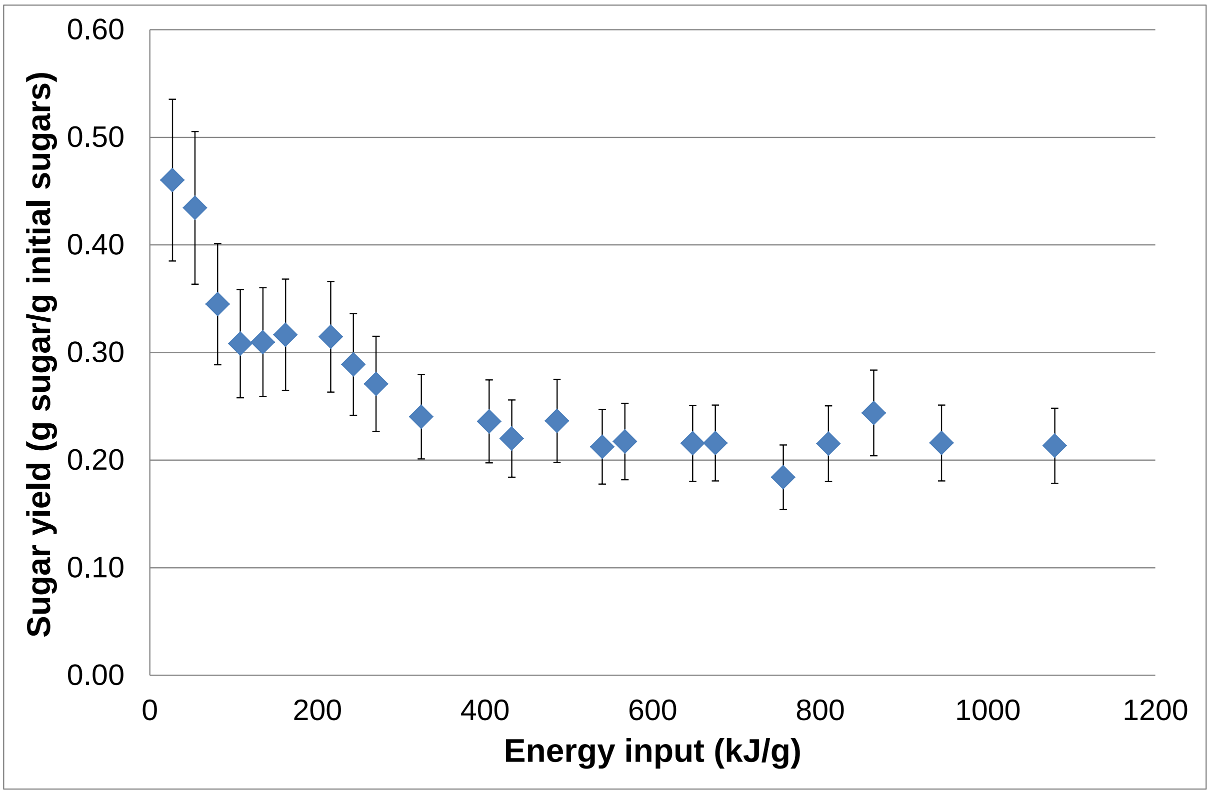

Figure 18: The effect of energy input on sugar yield using indirect sonication

The highest sugar yield of 0.15 ± 0.03 g sugar/g biomass (0.47 ± 0.08 g sugar/g available sugar) was achieved with an energy input of 27 kJ/g. This corresponds well with the 0.13 g sugar/g biomass found by Abidin *et al.* (2011) using ultrasound (100% power, 20 minutes, 10 w/v% biomass loading, direct probe).

The effect of pretreatment time at the various power settings are shown in Figure 19. It can clearly be seen that a longer pretreatment time results in higher sugar yields. A lower power input over a longer pretreatment time will thus liberate more sugars than an increased power input with a shorter pretreatment time.

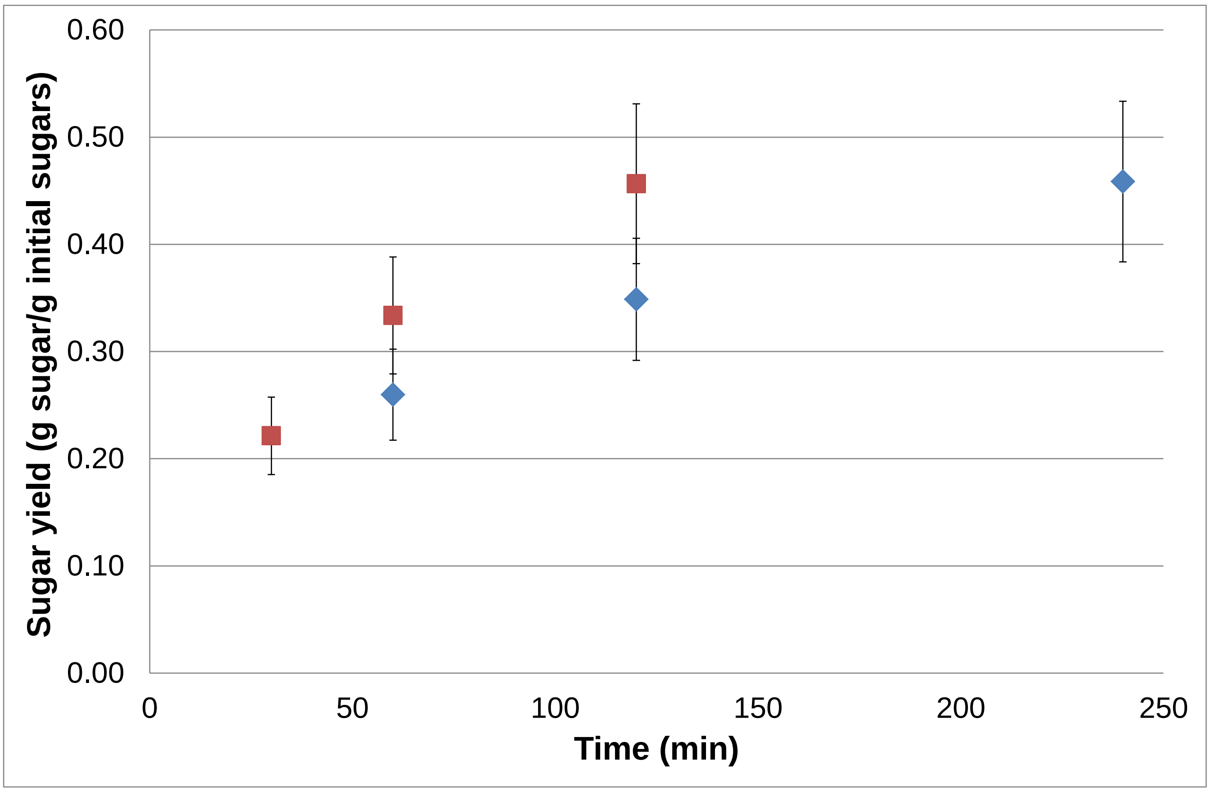

Figure 19: The effect of pretreatment time on sugar yield with indirect sonication (◆ 216 kJ/g, ■ 108 kJ/g)

4.5.2 *Pretreatment using direct sonication*

The effect of different energy input on the liberation of sugars from water hyacinth biomass using direct sonication is shown in Figure 20. Direct sonication generally showed less sugars liberated than indirect sonication. Sugar yields varied between 0.072 and 0.091 ± 0.008 g sugar/g biomass (0.237 and 0.262 ± 0.024 g sugar/g initial sugar). With an increase in energy input there is an increase in the degradation of the sugars during ultrasonic pretreatment (Abidin *et al.*, 2011).

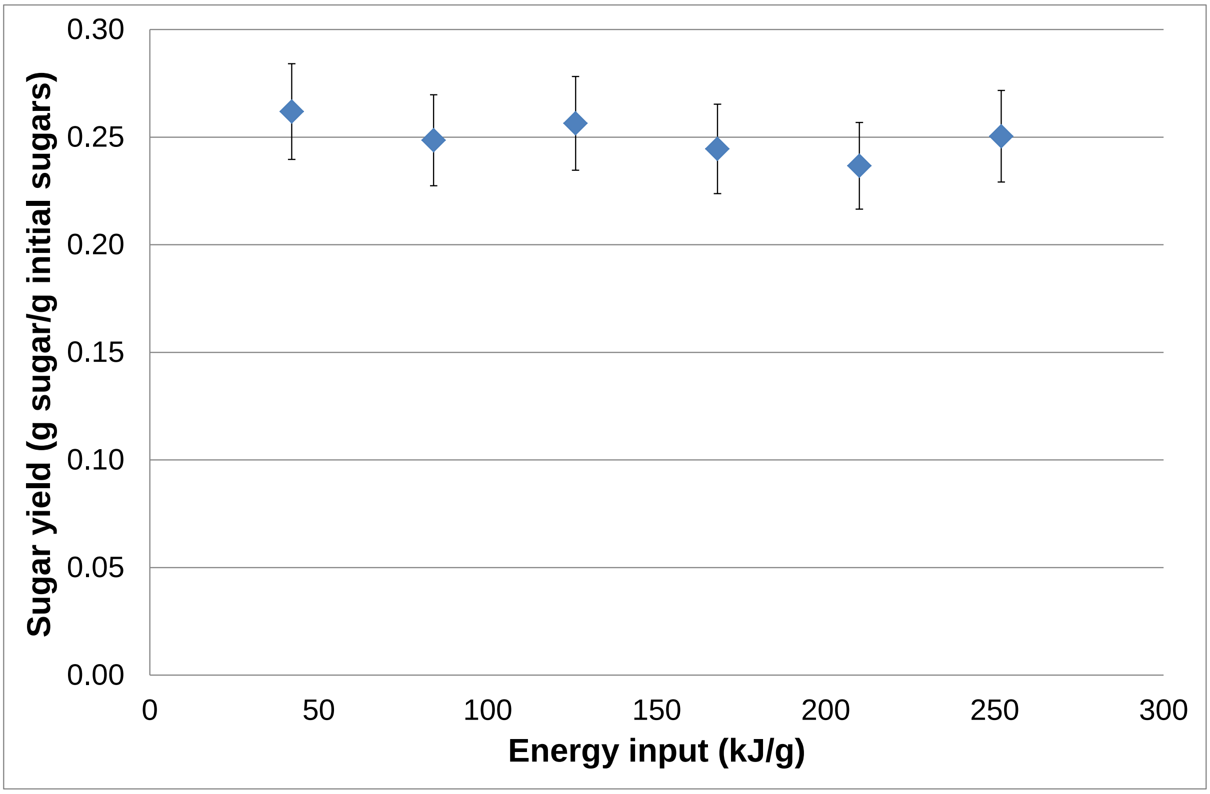

Figure 20: The effect of energy input on sugar yield using a direct probe

4.5.3 FTIR analysis

FTIR analysis was done on untreated biomass, as well as alkali pretreated water hyacinth using indirect and direct sonication. A Shimadzu IRAffinity-1 Fourier Transform Infrared Spectrophotometer (FTIR) was used for these analyses. FTIR analysis showed changes to the functional groups in the biomass before and after pretreatment. A wavelength in the range of 4000 cm^{-1} to 450 cm^{-1} was used to analyse the samples with regards to the transmittance. The most prominent peaks related to the given biomass are given in Table 17 .

Table 17: Prominent peaks related to biomass pretreatment (Binod *et al*., 2012)

Wavenumbers (cm^{-1})	**Description**
3350 – 3500	The O-H stretching band of the hydroxyl group is usually associated with cellulose
2800 – 3000	The C-H stretching bands
2300 - 2500	CH_2-stretching
1500 – 1700	The aromatic C-C bending is coupled with hemicellulose
1400 – 1500	C=C stretching associated with the aromatic skeletal vibrations of the degradation of lignin
1050 – 1150	C-O-C stretching bands present represent glycosidic bonds, which is associated with the bonds between 5- and 6-carbon sugars

The results of the FTIR analysis are shown in Figure 21.

Figure 21: FTIR analysis of water hyacinth (— untreated, — direct sonication, — indirect sonication)

The peak at around 3350 - 3500 cm^{-1} indicates O-H stretching and is associated with cellulose. This indicates that the crystalline structure of the cellulose has not been fully disrupted. The broadening of the band after treatment indicates that some structural damage was done. The next prominent peak at around 2800 cm^{-1} shows stretching with methylene, which is associated with cellulose (Chen *et al.*, 2010).

The broad band between 1000 and 1200 cm^{-1} is indicative of the structure of cellulose and hemicellulose. The increase in band width could indicate that cellulose and hemicellulose are more exposed for enzymatic attack. Changes in the glycosidic band (900 - 910 cm^{-1}) indicate cleaving with the alkali. Two more peaks of importance are the peaks associated with the hemicellulose structure, found at 1740 cm^{-1} and 1245 cm^{-1} (Chen *et al.*, 2010).

The peaks at 1375 cm^{-1} and 1330 cm^{-1} are associated with bands generated due to cleavage of ether bonds in lignin. The C-H deformation in the methoxyl groups of lignin are associated with the peaks at 2860 cm^{-1}, 1460 cm^{-1} and 1425 cm^{-1}. Lastly, the peaks at 1610 cm^{-1} and 1516 cm^{-1} indicate aromatic skeletal vibrations in lignin (Chen *et al.*, 2010).

It can be concluded from the FTIR analysis that although more hemicellulose and cellulose are available for enzymatic hydrolysis following pretreatment, the bonds were not broken and the structure still remained intact. The liberation of the hemicellulose and cellulose can be explained by the breaking of the lignin bonds, which keep the structure intact. According to the spectra indirect sonication is more effective than direct sonication in the breaking of the lignin group bonds, thus resulting in more hemicellulose and cellulose being liberated.

4.5.4 Concluding remarks

Indirect sonication resulted in a higher sugar yield than that obtained using direct sonication. The reason for the higher sugar yield is the more efficient breakdown of the lignin and the subsequent liberation of the hemicellulose and cellulose, as confirmed by the FTIR results. Lower power input resulted in higher sugar yields, which can be ascribed to degradation of sugars at higher ultrasonic intensities.

The highest sugar yield for the indirect sonication pretreatment with 5% NaOH was found to be 0.15 g sugar/g biomass (0.47 g sugar/g available sugar) with an energy input of 27 kJ/g. Direct sonication delivered much lower sugar yields, varying between 0.237 and 0.262 g sugar/g initial sugar (0.072 and 0.091 g sugar/g biomass). The maximum theoretical ethanol yield of 0.24 g ethanol/g initial sugar (0.08 g ethanol/g biomass) that can be produced is much lower than the 0.19 g ethanol/g biomass reported by Chatterjee *et al.* (2012) and Ma *et al.* (2010) in two separate studies using water hyacinth as feedstock. Due to the high costs related to pretreatment and hydrolysis of water hyacinth to produce bioethanol, a similar conclusion is reached than Malik (2007), namely that water hyacinth as feedstock for bioethanol production should only be considered in circumstances where there is a very high requirement of ethanol as liquid fuel.

CHAPTER 5

5. THERMOCHEMICAL LIQUEFACTION

5.1 Introduction

In this chapter the bio-char and bio-oil yield obtained from the thermochemical liquefaction of water hyacinth feedstock is presented. The chemicals used in the thermochemical liquefaction experiments are described in Section 5.2. In Section 5.3 the experimental procedure is discussed while the results are presented in Section 5.4.

5.2 Chemicals

All the chemicals used during the thermochemical liquefaction of the water hyacinths, as well as the purpose of these chemicals, are shown in Table 18. The chemicals were used as provided by the supplier without any further purification.

Table 18: Chemicals used in during thermochemical liquefaction

Component	Details of components	Supplier	Purpose
Nitrogen	99.999% pure	Afrox	• Purging of autoclaves • Atmosphere during liquefaction
Carbon monoxide	99% pure	Afrox	Atmosphere during liquefaction
Carbon dioxide	99% pure	Afrox	Atmosphere during liquefaction
Chloroform	99% pure	ACE	Extraction of liquefaction products

5.3 Experimental procedure

A schematic representation of the experimental setup used during the thermochemical liquefaction is shown in Figure 22.

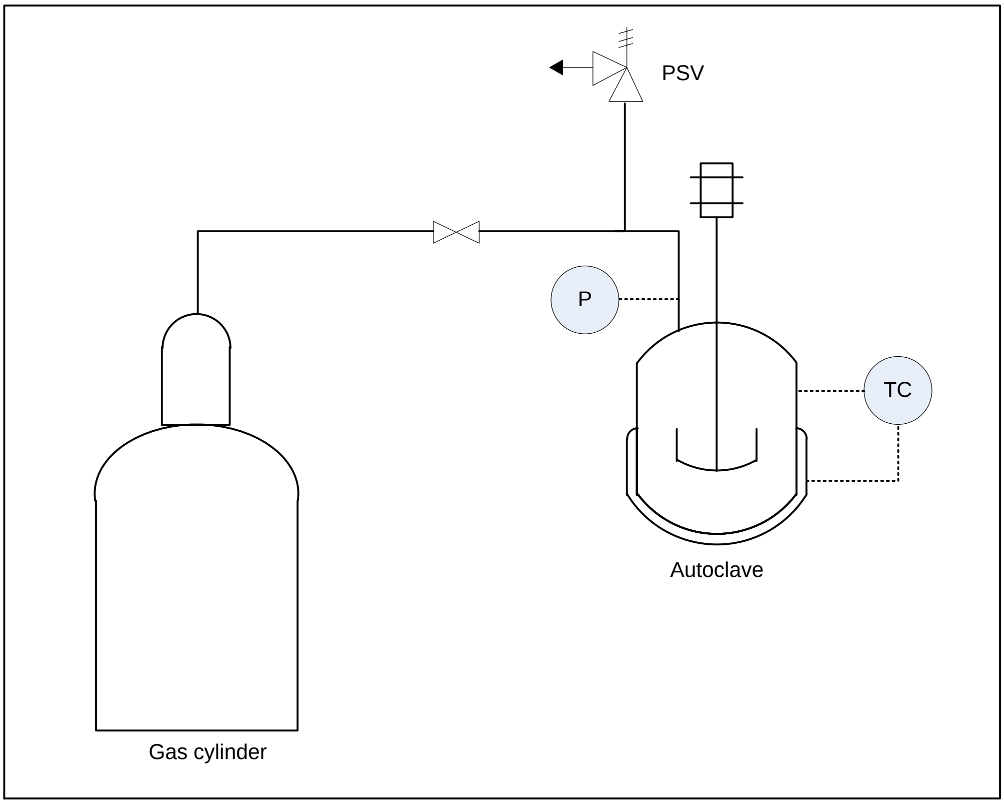

Figure 22: Schematic representation of experimental setup of thermochemical liquefaction

The material of construction of the autoclave is grade 316 stainless steel. A three-dimensional representation of the expanded autoclave is shown in Figure 23.

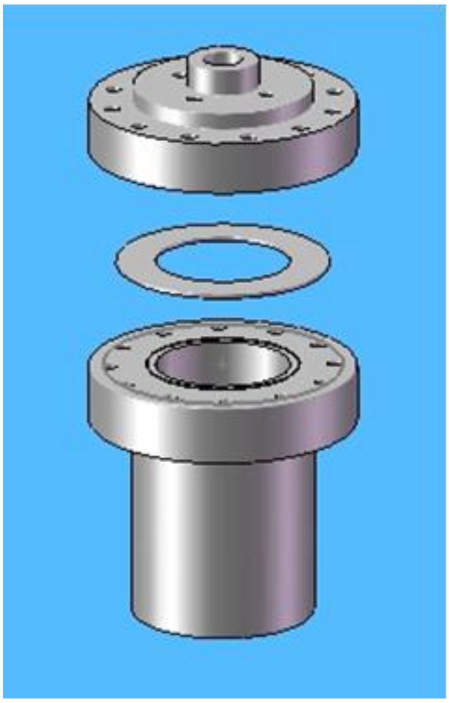

Figure 23: Three-dimensional representation of expanded autoclave

The inside diameter of the autoclave is 90 mm, the length 150 mm and the volume 954 mm^3. Thermochemical liquefaction was performed using both stems/leaves and roots. The experimental procedure was identical for both feedstock. An initial amount of 100 g and 50 g of biomass was weighed off for the roots and stems/leaves respectively. The biomass was then loaded into an autoclave, with a similar experimental setup as reported by Nigam (2002).

The autoclave was closed and the screw caps torqued shut to 70 Nm. The autoclave was purged and pressurised to 20 bar using Ultra High Purity (UHP) nitrogen. The purging step was repeated 5 times. The autoclave was then pressurized with the applicable atmosphere to 10 bar. A heating jacket was connected to the autoclave and the magnetic stirrer switched on.

The autoclave was heated at an average rate of 2.92 K/min. The residence time inside the autoclave was kept constant at 30 minutes. During this period the internal temperature was kept constant at the predetermined temperature setting using a temperature controller. The temperature dependent experiments were done with nitrogen as atmosphere for both feedstock, varying the temperatures between 240 and 340°C with intervals of 20°C. The atmosphere dependent experiments were done with carbon monoxide, nitrogen and carbon dioxide as atmosphere.

Upon completion of the liquefaction process, the autoclave was cooled down to room temperature. The products were extracted from the autoclave with 100 ml chloroform. The chloroform was poured into the autoclave after which the autoclave was closed and the magnetic stirrer switched on for 10 minutes. The bio-char was then filtered off in a vacuum filtration setup, weighed and dried over night at 105°C. A summary of the experimental procedure is shown in Figure 24.

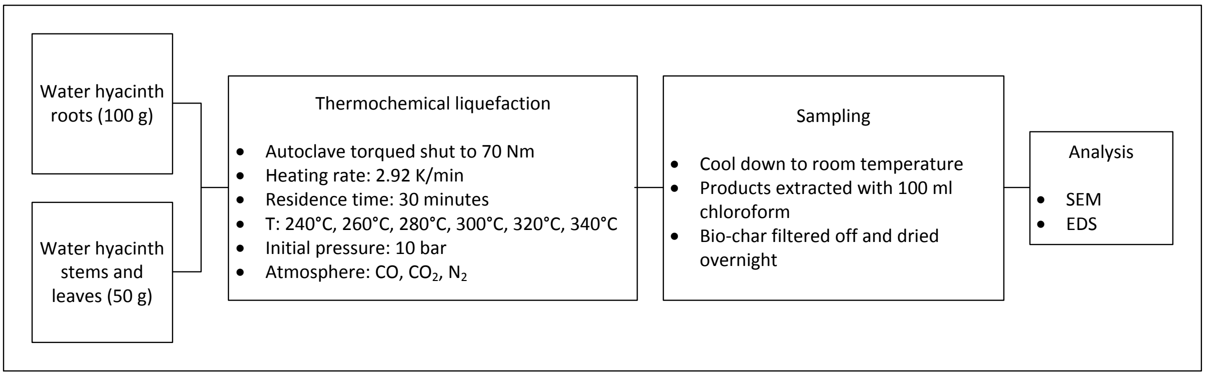

Figure 24: Summary of experimental procedure during liquefaction

5.3.1 Analysis

The bio-char was analysed with a scanning electron microscope (SEM), as well as with energy dispersive X-ray spectroscopy (EDS). These analyses were performed to determine the degree to which the biomass was charred, as well as to find the carbon to oxygen ratio of the bio-char.

5.4 Results

5.4.1 Temperature

The temperature dependent experiments were done with nitrogen as atmosphere for both the roots and the stems and leaves, varying the temperatures between 240°C and 340°C with intervals of 20°C. First of all the extent of liquefaction is considered by looking at the scanning electron microscope (SEM) results of the biomass in Figure 25 and Figure 26.

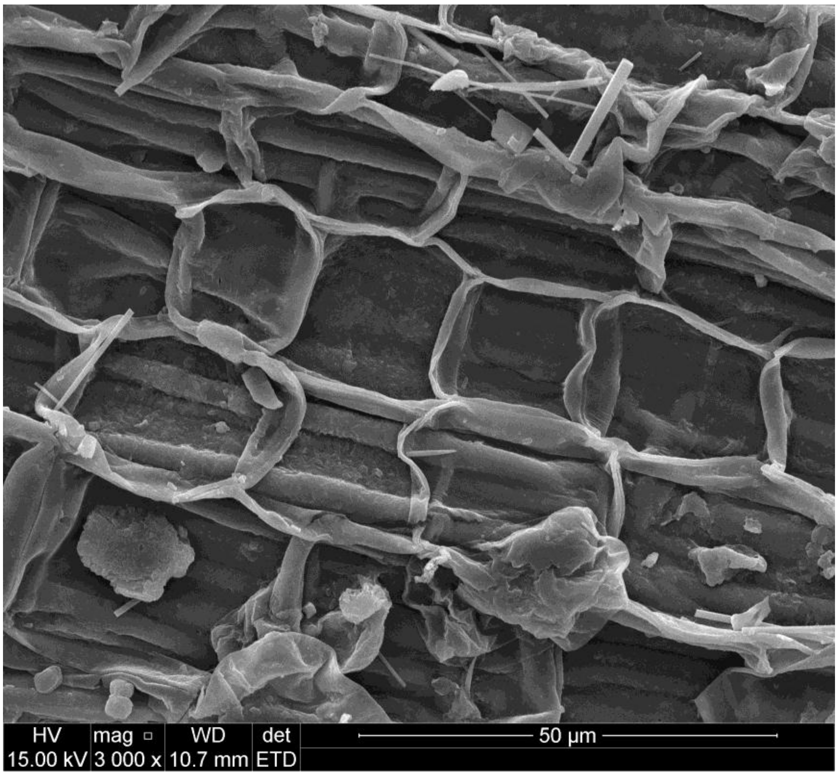

Figure 25: SEM image showing the untreated water hyacinth

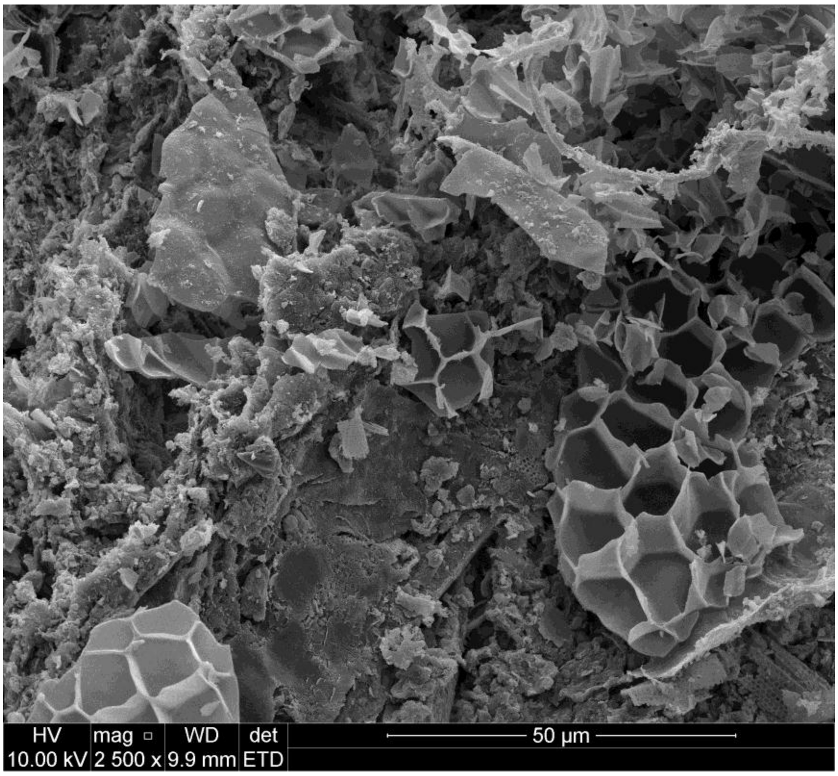

Figure 26: SEM image showing the effect of temperature on the extent of charring at 240°C

The SEM images show that at 240°C the biomass is not completely charred. Although partial damage has occurred at 240°C, the cell structure is still mostly intact if compared to the fresh biomass. In Figure 27 the extent of liquefaction at 260°C is shown. All cell structures that were still clearly visible at 240°C have been damaged at this higher temperature, showing that the minimum temperature at which complete charring occurs is 260°C.

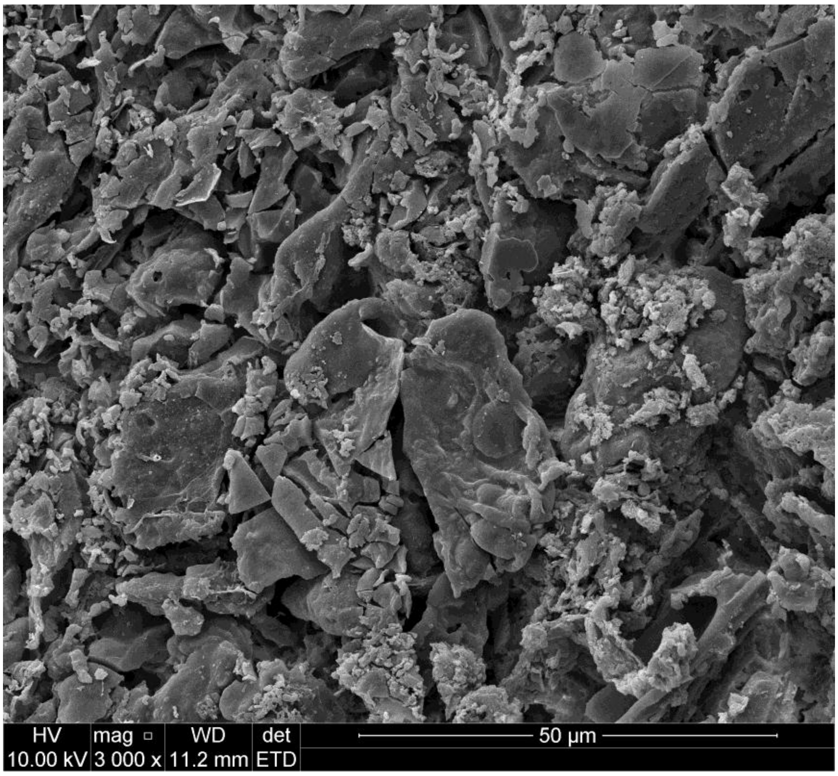

Figure 27: SEM image showing the effect of temperature on the extent of charring at 260°C

The effect of the liquefaction temperature on the bio-char yield is shown in Figure 28. There is a decline in the bio-char yield as the liquefaction temperature increases. At higher temperatures volatile components are released, resulting in a lower solid residue. Higher temperatures favour oil-yields, while hydrocracking starts to occur at temperatures in excess of 300°C (Koguchi *et al.*, 1987).

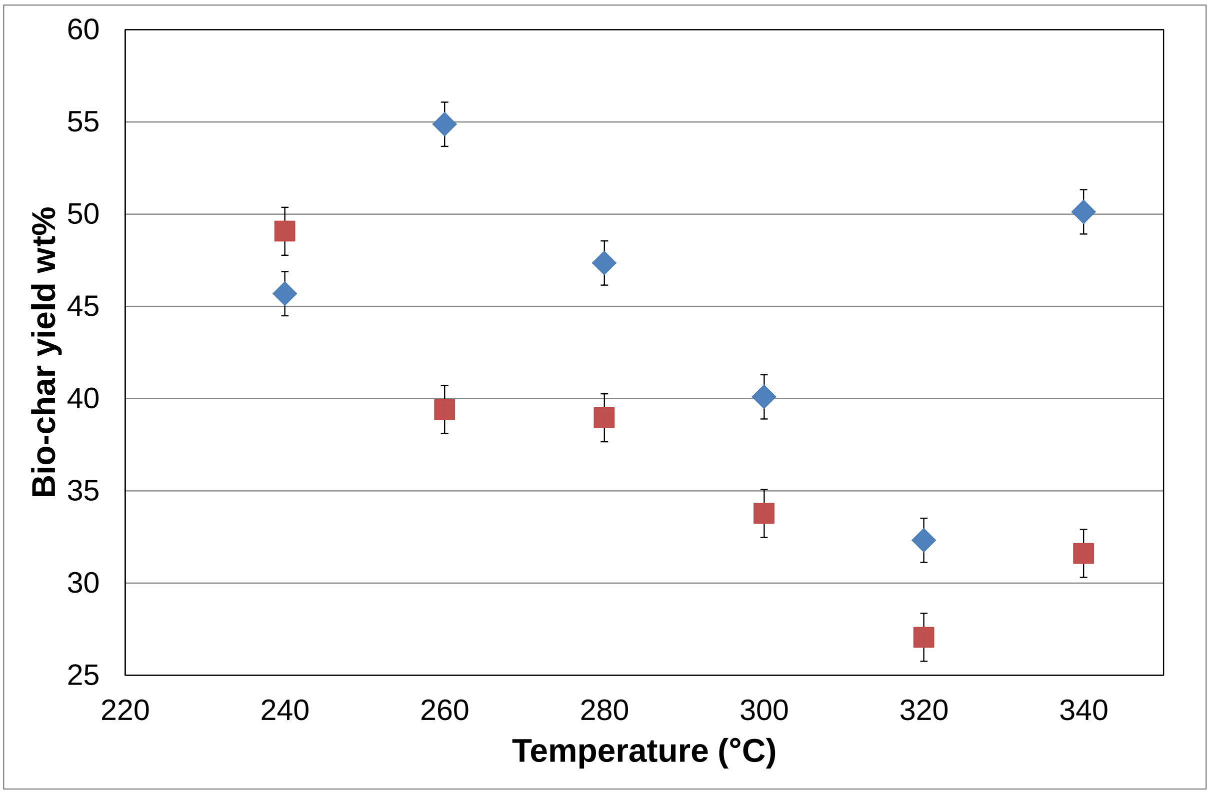

Figure 28: Effect of temperature on bio-char yield during thermochemical liquefaction (🟥 roots, ◆ stems and leaves)

An optimum bio-char yield of 54.9 ± 3.4 wt% was reached for the stems and leaves at 260°C. The highest yield for the roots, on the other hand, of 49.1 ± 3.2 wt% was reached at 240°C. It was already established by examining the SEM images that the charring process was not fully completed at 240°C, thus the optimum yield for the roots was in actual fact only 39.4 ± 3.2 wt%.

The increase in bio-char yield at 340°C was found to be inconsistent with the other results. At this temperature, however, the process is technically not classified as liquefaction anymore, but as pyrolysis (Rosendahl *et al.*, 2011). A possible explanation for the higher bio-char yield might be the formation of different compounds during the pyrolysis process, including waxes and oils. The effect of the temperature on the carbon to oxygen ratio of the bio-char is shown in Table 19 using carbon monoxide in the case of the roots and nitrogen in the case of the stems and leaves, as these atmospheres gave the highest C/O values for the respective feedstock.

Table 19: Carbon to oxygen ratio at different temperatures

Feedstock	**Liquefaction temperature (°C)**	**C/O**
Roots	Raw feed	0.78
	240	1.02
	320	1.18
Stems and leaves	Raw feed	1.07
	240	3.26
	320	3.78

There was an increase in the C/O ratio after liquefaction, as was expected, because both deoxygenisation and liquefaction occur at the same time. This is due to the dissociation of the O-H bonds and the recombination into hydrocarbons (Li *et al*., 2012). There was, however, a much larger increase in the C/O ratio in the case of the stems and leaves than with the roots. This can be explained by the lower initial protein, fat and carbohydrates content of the roots.

5.4.2 Liquefaction atmosphere

The atmosphere dependent experiments were done using carbon monoxide, nitrogen and carbon dioxide as atmosphere for both the feedstock. The effect of the use of different atmospheres in the case of the roots is shown in Figure 29.

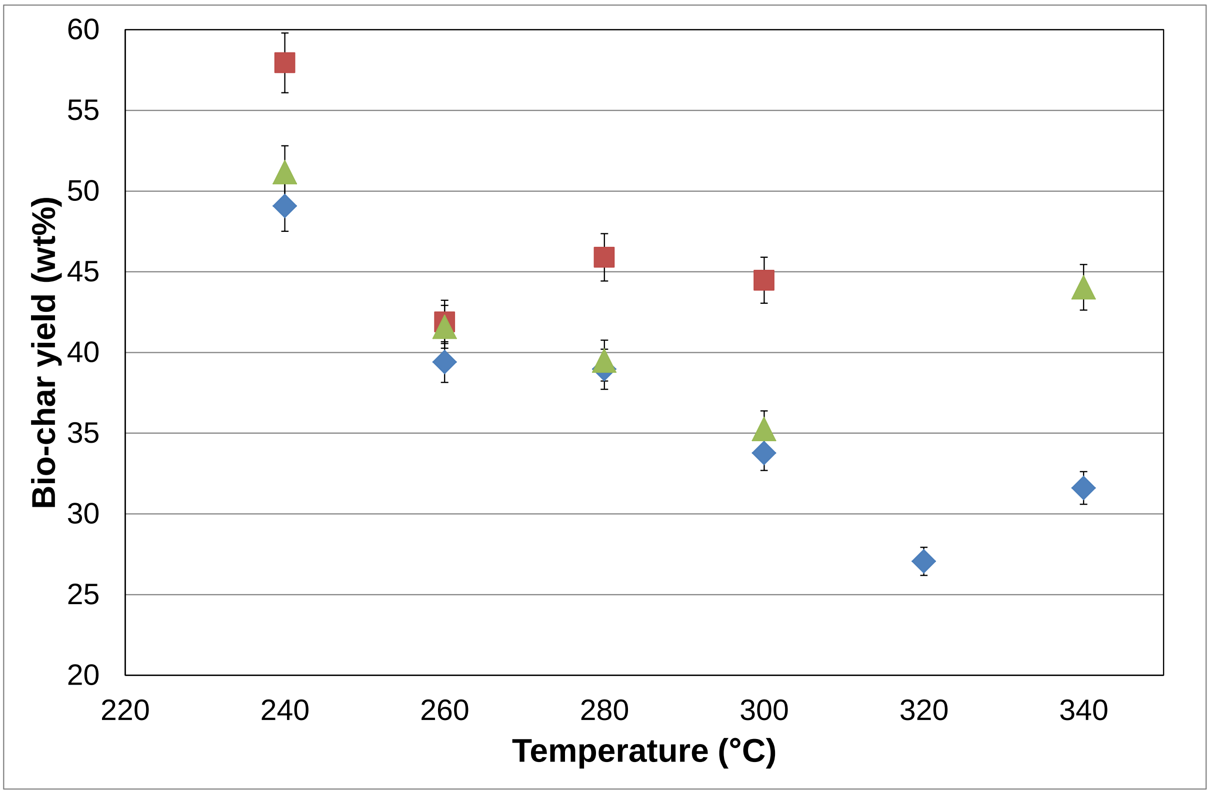

Figure 29: Effect of atmosphere on bio-char yield using roots as feedstock (■ carbon monoxide, ◆ nitrogen, ▲ carbon dioxide)

The highest average yield was obtained with carbon monoxide (non-reducing) as atmosphere, followed by carbon dioxide (stronger non-reducing) and nitrogen (inert). This is expected as carbon monoxide and carbon dioxide are not a reducing gas, while nitrogen is an inert gas. Due to complete charring only occurring above 240°C, the results at 240°C do not reflect the actual bio-char yield. Furthermore, the results above 320°C are also discarded, as this is within the pyrolysis range. The highest bio-char yields of 45.9 ± 3.2 wt% (280°C), 41.6 ± 3.2 wt% (260°C) and 39.4 ± 3.2 wt% (260°C) were obtained for the carbon monoxide, carbon dioxide and nitrogen, respectively. Carbon monoxide was thus found to be the ideal atmosphere during the liquefaction of water hyacinth roots. Barnard (2009) found that biomass with insufficient hydrogen content, which might be the case with the water hyacinth roots due to the low hydrocarbon, protein and fat content, requires a reducing atmosphere for optimum liquefaction yields.

Opposite results were found when the stems and leaves were used during the liquefaction experiments, as shown in Figure 30.

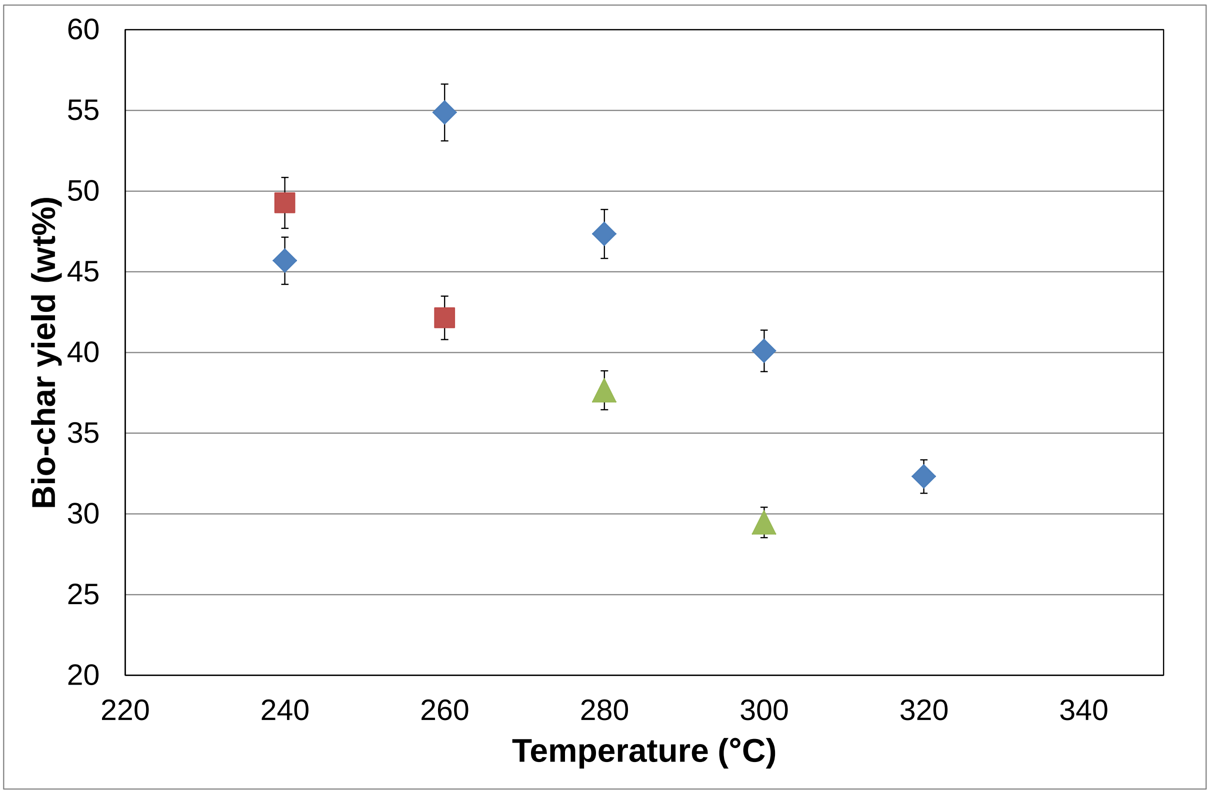

Figure 30: Effect of atmosphere on bio-char yield using stems and leaves as feedstock (■ carbon monoxide, ◆ nitrogen, ▲ carbon dioxide)

Again excluding all values below 240°C and above 320°C, the highest bio-char yields of 42.2 ± 3.2 wt% (260°C), 37.7 ± 3.2 wt% (280°C) and 54.9 ± 3.2 wt% (260°C) were obtained for the carbon monoxide, carbon dioxide and nitrogen, respectively. With carbon monoxide and carbon dioxide as atmospheres the optimum bio-char yields were lower than during the experiments where roots were used as feedstock. There was, however, a considerable increase in the bio-char yield when nitrogen was used as atmosphere.

The optimum atmosphere for liquefaction of stems and leaves is thus nitrogen. This might be indicative of low hydrogen content in the raw biomass, seeing as both the carbon monoxide and carbon dioxide are non-reducing gases. In the absence of a reducing gas a lower yield means that low hydrogen shutting occurred. It is thus recommended to further investigate the bio-char yields at different reducing atmospheres, such as hydrogen.

The effect of the temperature on the carbon to oxygen ratio of the bio-char is shown in Table 20. The initial C/O ratio of the roots was 0.78.

Table 20: Carbon to oxygen ratio at different atmospheres for the roots

Atmosphere	Liquefaction temperature (°C)	C/O
Carbon monoxide	240	1.02
	320	1.19
Carbon dioxide	240	1.42
	300	1.34
Nitrogen	240	0.83
	320	0.78

There is an increase in the initial C/O ratio when using the non-reducing gases, carbon monoxide and carbon dioxide, as atmosphere. This shows that there was a degree of deoxygenation that took place during liquefaction. The experiments using nitrogen as atmosphere showed little or no change in the C/O ratio.

5.4.3 Higher heating value of the bio-char

The higher heating value (HHV) of the bio-char was determined to be 10.89 ± 0.45 MJ/kg for the roots and 23.31 ± 0.45 MJ/kg for the stems and leaves. The HHV of the roots is less than 50% of the HHV of the stems and leaves. The low HHV of the roots can be explained by its composition, as well as by the nature of the plant to extract heavy metals from water. These impurities remain in the roots after harvesting. The HHV of the stems and leaves is within the range of the CV for coal, which suggests that the bio-char can be used as solid bio-fuel in industrial processes.

5.4.4 Bio-oil yield

The biomass loading was kept constant at 8% and 23% respectively for the roots and the stems and leaves. Extraction chemicals, namely acetone and chloroform, were investigated to see if it would be possible to extract any bio-oil. Due to the low biomass loading the bio-oil yield was found to be too low to accurately quantify.

5.4.5 Conclusions

The optimum bio-char yield of 54.9 ± 3.4 wt% (0.55 g bio-char/g biomass) was achieved using a nitrogen atmosphere at 260°C and the stems and leaves as feedstock. With the roots a slightly lower optimum yield of 45.9 ± 3.2 wt% (0.46 g bio-char/g biomass) was found using carbon monoxide as atmosphere at 280°C. The results of the various experiments are summarised in Table 21.

Table 21: Optimum bio-char yields for various temperatures and atmospheres

	CO		CO_2		N_2	
Feedstock	**Bio-char yield (wt%)**	**Optimum temperature (°C)**	**Bio-char yield (wt%)**	**Optimum temperature (°C)**	**Bio-char yield (wt%)**	**Optimum temperature (°C)**
Stems and leaves	42.2	260	37.7	280	54.9	260
Roots	45.9	280	41.6	260	39.4	260

Nitrogen was found to be the optimum atmosphere for liquefaction of the stems and leaves, while carbon monoxide was the optimal atmosphere using roots as feedstock. The increase in the C/O ratio during the experiments with carbon monoxide and carbon dioxide indicate that deoxygenation occurred during liquefaction. The nitrogen experiments showed negligible change in the C/O ratio. Lastly, a HHV of 10.89 ± 0.45 MJ/kg and 23.31 ± 0.45 MJ/kg were achieved for the roots and the stems and leaves, respectively. The HHV of the stems and leaves is comparable to that of coal and thus ideal to be used as solid bio-fuel.

CHAPTER 6

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Introduction

In this study the potential of water hyacinth as feedstock for bio-energy production was evaluated. This study focused on the production of ethanol-gel, the ultrasonic pretreatment of the water hyacinth for bio-ethanol production, the thermochemical liquefaction of the biomass, as well as the extraction of water from the biomass. The conclusions and recommendations are presented in this chapter.

6.2 Conclusions

The average moisture content of the *Eichhornia crassipes* was found to be 93.24 ± 0.75 wt%. This is one of the major challenges in using water hyacinth as feedstock. Both in the production of ethanol-gel and in the ultrasonic pretreatment of the biomass a water removal step was required. This results in additional costs during production.

As South Africa is an arid country, the responsible utilisation of water is of the utmost importance. In order to address the challenge of the high moisture content in the biomass, the extraction of water from the water hyacinth was evaluated. Water could successfully be extracted from water hyacinth using enzymatic and chemical additives. From a cost and simplicity perspective, it was concluded that Pectinex Ultra SP-L (pH = 3.5; T = 40°C) is the optimum extraction agent, giving a water yield of 0.88 ± 0.01 $g_{water}/g_{water\ in\ biomass}$. The added de-ionised successfully water lowered the viscosity and increased the contact area between the enzymes and the biomass, resulting in higher water yields. The high TDS, magnesium and potassium levels should however be reduced by further treatment before the extracted water will be suitable for domestic, industrial or agricultural application.

The remaining biomass after water extraction was successfully used in the production of ethanol-gel, as well as in the ultrasonic pretreatment of the biomass. The ethanol-gel was successfully produced using 90 vol% ethanol and 10 vol% water. The higher heating value (HHV) of the ethanol-gel was found to be 17.6 MJ/kg. The ethanol-gel produced from water hyacinth was compared to the standard for ethanol-gel, as specified in SANS 448. The ethanol-gel was found to ignite readily and burn steadily, without flaring, sudden deflagrations, sparking, splitting, popping, dripping or exploding from ignition until it had burned to extinction, as required by SANS 448.

The only specifications that could not be met were the viscosity and the high waste residue after burning. The costs involved with the manufacturing of ethanol-gel from water hyacinth are extremely high. It can be concluded that ethanol-gel cannot be economically produced using water hyacinth as feedstock.

The second biofuel under consideration was bio-ethanol, with the specific focus on the ultrasonic pretreatment of water hyacinth to produce fermentable sugars. Indirect sonication in an ultrasonic bath proved to be a better pretreatment method than the direct sonication with an ultrasonic probe. It was further found that a longer pretreatment time at a lower power setting was more beneficial than a higher power setting and a short sonication time. The more efficient breakdown of cellulose and hemicellulose by means of indirect sonication was confirmed by the FTIR results. Lower power input resulted in higher sugar yields, which can be ascribed to degradation of sugars at higher ultrasonic intensities.

The optimum sugar yield for the ultrasonic bath pretreatment with 5% NaOH was found to be 0.15 g sugar/g biomass (0.47 g sugar/g available sugar) was achieved with an energy input of 27 kJ/g. The optimum theoretical ethanol yield of 0.24 g ethanol/g initial sugar (0.08 g ethanol/g biomass) that can be produced is extremely low compared to other pretreatment methods.

Lastly, bio-char and bio-oil via thermochemical liquefaction was considered. One of the advantages of this process is that the water hyacinth biomass need not be dried to the same extent as was the case with the ethanol-gel and the ultrasonic pretreatment, as water is one of the reagents in the system. The optimum bio-char yield of 54.9 ± 3.4 wt% was achieved using a nitrogen atmosphere at 260°C and the stems and leaves as feedstock. The roots produced a slightly lower optimum yield of 45.9 ± 3.2 wt% using carbon monoxide as atmosphere at 280°C.

Nitrogen was found to be the optimum atmosphere for liquefaction of the stems and leaves, while carbon monoxide was the optimal atmosphere using roots as feedstock. A higher heating value (HHV) of 10.89 ± 0.45 MJ/kg and 23.31 ± 0.45 MJ/kg were achieved for the roots and the stems and leaves, respectively. The HHV of the stems and leaves is comparable to the CV of coal and thus ideal to be used as solid bio-fuel.

In order to reach a final conclusion on the suitability of water hyacinth as feedstock for bio-energy production, a comparison between the various bio-energy options is made in Table 22.

Table 22: Comparison between various bio-energy production routes for water hyacinth

	Ethanol-gel	**Bio-ethanol**	**Bio-char**
Extensive water removal	Required	Required	Not required
Higher heating value (MJ/kg)	17.6	29.7	23.3
Product yield (g product/g biomass)	0.1	0.08	0.55
Energy yield (MJ/kg biomass)	1.8	2.4	12.8

Based on this comparison the ethanol-gel route would result in the lowest possible energy yield of just 1.8 MJ/kg biomass, followed by the bio-ethanol production of 2.4 MJ/kg. Both these production routes require water removal prior to energy production. It would seem as if ethanol-gel would thus be the most unlikely route, due to the cost of the chemical additives, the cost of the addition of ethanol to the alkaline cellulose to produce the gel, as well as the production cost.

The simplest route to follow is thermochemical liquefaction. Bio-char as bio-fuel results in the highest energy yield of all investigated products. Not only is no pretreatment required, but the cost of additives is also lower than that of the ethanol-gel and bio-ethanol. The overall energy yield based on the water hyacinth biomass is, however, very low compared to other fuel sources. Furthermore, the cost involved with heating the biomass to the required temperatures during liquefaction is also quite high.

In conclusion, the use of water hyacinth as feedstock for biofuel production is an expensive exercise due to the high water content of the biomass. Based on this study the most optimum biofuel from water hyacinth is bio-char. It is, however, only recommended to use this biomass as a feedstock for biofuel if no alternative feedstock are available.

6.3 Recommendations

There is still a need to further investigate ultrasonic pretreatment in order to better understand the mechanism involved during pretreatment. There should be thus focussed on the hydrolysis and fermentation of the sugars derived from the water hyacinth. Furthermore, the potential of water hyacinth as feedstock for bio-gas, compost and animal feed, as well as material for the removal of heavy metals from water systems should also be investigated to fully be able to evaluate water hyacinth as a feedstock, not only for bio-energy production, but also for alternative applications.

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APPENDIX A

A.1 Experimental error

In this section the methodology that was used to calculate the experimental errors for the various experiments are discussed. All experiments were repeated at least three times with identical operating conditions. A 95% confidence interval was used as basis for the calculations, assuming a normal distribution of the experimental values.

First of all, the mean is calculated using the following equation:

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \qquad (A.1)$$

with n the total number of data points and x_i an individual data point. Secondly, the standard deviation is calculated for the data set:

$$s = \sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \div (n-1)} \qquad (A.2)$$

with s the standard deviation. Thirdly, the standard error of the mean is calculated:

$$Standard\ error\ of\ the\ mean = SE = \frac{s}{\sqrt{n}} \qquad (A.3)$$

Fourthly, the z-critical value for the 95% confidence interval is calculated as follows:

$$z = (\bar{x} - \mu) \div \frac{s}{\sqrt{n}} \qquad (A.4)$$

with µ the mean value for the continuous variable, x. The confidence interval is calculated next using the following equation:

$$Confidence\ interval = \bar{x} \pm (SE \times z) \qquad (A.5)$$

Finally, the experimental error is calculated as follows:

$$Experimental\ error = \frac{2 \times Confidence\ interval}{\bar{x}} \times 100 \qquad (A.6)$$

A.2 Water extraction experiments

Table 23: Moisture content of wet and dried water hyacinth

Sample number	Wet biomass (g)	Dry biomass (g)	Moisture content (wt%)
1	100	7.5	92.5
2	100	6.8	93.2
3	100	5.8	94.2
4	100	6.9	93.1
5	100	6.8	93.2
Average	**100**	**6.8**	**93.2**

Table 24: Optimum oven time for the various additives

Additive	Oven time (hours)	Water yield (total biomass) (wt%)	Water yield (total water content) (wt%)
Celluclast	1	68.1	73.0
	2	66.7	71.5
	3	68.7	73.7
	4	66.2	71.0
	5	68.7	73.7
Pectinex	1	62.7	67.2
	2	61.7	66.2
	3	63.7	68.3
	4	60.7	65.1
	5	56.7	60.8
Tween 80	1	56.7	60.8
	2	56.7	60.8
	3	57.7	61.9
	4	55.7	59.7
	5	56.7	60.8

Table 25: Influence of pH on water yield

Additive	pH	Water yield (total biomass) (wt%)	Water yield (total water content) (wt%)
Celluclast	2.5	58.7	63.0
	3.5	62.9	67.5
	4.5	63.9	68.5
	5.5	66.7	71.5
	6.5	60.2	64.6
Pectinex	2.5	56.7	60.8
	3.5	62.1	66.6
	4.5	61.4	65.8
	5.5	60.9	65.3
	6.5	58.7	63.0
Tween 80	2.5	57.7	61.9
	3.5	59.7	64.0
	4.5	61.3	65.7
	5.5	60.1	64.5
	6.5	55.6	59.6

Table 26: Influence of temperature on water yield

Additive	Temperature (°C)	Water yield (total biomass) (wt%)	Water yield (total water content) (wt%)
Celluclast	30	57.7	61.9
	35	75.5	81.0
	40	73.9	79.2
	45	73.0	78.3
	50	70.7	75.9
Pectinex	30	59.7	64.0
	35	61.7	66.2
	40	75.2	80.7
	50	73.9	79.3
Tween 80	30	55.7	59.7
	35	70.2	75.2
	40	69.5	74.6
	45	68.8	73.8
	50	65.6	70.3

Table 27: Influence of pH on water yield with combination of Celluclast 1.5 L and Pectinex Ultra SP-L

pH	Water yield (total biomass) (wt%)	Water yield (total water content) (wt%)
2.5	73.7	79.0
3.5	77.7	83.3
4.0	79.8	85.5
4.5	78.7	84.4
5.5	75.7	81.2
6.5	70.7	75.8

Table 28: Influence of temperature on water yield with combination of Celluclast 1.5 L and Pectinex Ultra SP-L

Temperature (°C)	Water yield (total biomass) (wt%)	Water yield (total water content) (wt%)
30	72.2	77.4
35	73.7	79.0
37.5	76.8	82.4
40	74.7	80.1
45	72.6	77.9
50	71.7	76.9

Table 29: Influence of the addition of de-ionised and recycled extracted water

Additive	**Maximum water yield without additional water (wt%)**	**Maximum water yield with additional de-ionised water (wt%)**
Celluclast	79.2	84.4
Pectinex	79.3	87.8
Tween 80	75.2	81.0
Celluclast & Pectinex	85.5	88.7

Table 30: Analysis of extracted unfiltered water

Parameter	**Sample 1**	**Sample 2**	**Sample 3**	**Average**	**Experimental error**
TDS (mg/L)	8951	8892	8977	8940	79.5
Total hardness (mg/L)	128	133	128	130	5.4
SAR	0.36	0.35	0.36	0.36	0.01
Potassium	371	376	381	376	9
Sodium	12.8	12.5	13.1	12.8	0.6
Phosphates	107.6	104.1	101.2	104.3	5.9
Manganese	7.2	7.9	7.4	7.5	0.6

Table 31: Analysis of extracted filtered water

Parameter	**Sample 1**	**Sample 2**	**Sample 3**	**Average**	**Experimental error**
TDS (mg/L)	8951	8892	8977	8940	79.5
Total hardness (mg/L)	2.4	2.4	2.4	2.4	0.1
Potassium	91	94	101	96	10
Sodium	9.2	9.7	10.4	9.7	0.4
Phosphates	25.2	22.6	21.3	23.0	3.7
Manganese	0.1	0.1	0.1	0.1	0.01

A.3 Ultrasonic fermentation experiments

Table 32: Areas obtained during pretreatment (ultrasonic bath)

Power input (W)	Time	Energy input (kJ)	Area				
			Mannose	Fructose	Glucose	Xylose	Cellubiose
150	30	270	0	0	0	0	136000
150	60	540	0	0	0	0	139000
150	90	810	0	0	0	0	136000
150	120	1080	0	0	0	0	138000
150	150	1350	0	0	0	0	142000
150	180	1620	0	0	0	0	138000
150	210	1890	0	0	0	0	138000
150	240	2160	0	0	0	0	143000
300	30	540	14457	0	0	0	96284
300	60	1080	3519	0	0	0	93867
300	90	1620	0	0	0	0	97367
300	120	2160	389	387	0	0	104101
300	150	2700	474	0	0	0	106984
300	180	3240	0	0	0	0	98991
300	210	3780	0	0	0	0	103367
300	240	4320	0	0	0	0	44701
450	30	810	0	1732	0	0	92433
450	60	1620	0	667	0	0	73819
450	90	2430	1070	619	0	0	100744
450	120	3240	0	0	0	0	75769
450	150	4050	631	0	0	0	72551
450	180	4860	803	0	0	0	74035
450	210	5670	1009	0	0	0	76574
450	240	6480	1103	0	0	0	69146
600	30	1080	570	0	0	0	75190
600	60	2160	860	668	0	0	74762
600	90	3240	0	0	0	0	73149
600	120	4320	0	1407	0	0	71689
600	150	5400	0	0	0	0	71816
600	180	6480	0	0	0	0	75607
600	210	7560	0	0	0	0	42858
600	240	8640	0	0	0	0	84311
750	30	1350	0	0	0	0	80008
750	60	2700	1094	0	0	0	79370
750	90	4050	0	0	0	0	70664
750	120	5400	674	0	0	0	71481
750	150	6750	0	0	0	0	77708
750	180	8100	789	0	0	0	72592

Table 33: Sugar concentrations after pretreatment (ultrasonic bath)

Power input (W)	Time	Energy input (kJ)	Concentration (g/L)				
			Mannose	Fructose	Glucose	Xylose	Cellubiose
150	30	270	0.00	0.00	0.00	0.00	7.58
150	60	540	0.00	0.00	0.00	0.00	7.75
150	90	810	0.00	0.00	0.00	0.00	7.58
150	120	1080	0.00	0.00	0.00	0.00	7.69
150	150	1350	0.00	0.00	0.00	0.00	7.92
150	180	1620	0.00	0.00	0.00	0.00	7.69
150	210	1890	0.00	0.00	0.00	0.00	7.69
150	240	2160	0.00	0.00	0.00	0.00	7.97
300	30	540	1.25	0.00	0.00	0.00	5.37
300	60	1080	0.31	0.00	0.00	0.00	5.23
300	90	1620	0.00	0.00	0.00	0.00	5.43
300	120	2160	0.03	0.04	0.00	0.00	5.80
300	150	2700	0.04	0.00	0.00	0.00	5.96
300	180	3240	0.00	0.00	0.00	0.00	5.52
300	210	3780	0.00	0.00	0.00	0.00	5.76
300	240	4320	0.00	0.00	0.00	0.00	2.49
450	30	810	0.00	0.18	0.00	0.00	5.15
450	60	1620	0.00	0.07	0.00	0.00	4.12
450	90	2430	0.09	0.06	0.00	0.00	5.62
450	120	3240	0.00	0.00	0.00	0.00	4.22
450	150	4050	0.05	0.00	0.00	0.00	4.04
450	180	4860	0.07	0.00	0.00	0.00	4.13
450	210	5670	0.09	0.00	0.00	0.00	4.27
450	240	6480	0.10	0.00	0.00	0.00	3.85
600	30	1080	0.05	0.00	0.00	0.00	4.19
600	60	2160	0.07	0.07	0.00	0.00	4.17
600	90	3240	0.00	0.00	0.00	0.00	4.08
600	120	4320	0.00	0.15	0.00	0.00	4.00
600	150	5400	0.00	0.00	0.00	0.00	4.00
600	180	6480	0.00	0.00	0.00	0.00	4.22
600	210	7560	0.00	0.00	0.00	0.00	2.39
600	240	8640	0.00	0.00	0.00	0.00	4.70
750	30	1350	0.00	0.00	0.00	0.00	4.46
750	60	2700	0.09	0.00	0.00	0.00	4.42
750	90	4050	0.00	0.00	0.00	0.00	3.94
750	120	5400	0.06	0.00	0.00	0.00	3.99
750	150	6750	0.00	0.00	0.00	0.00	4.33
750	180	8100	0.07	0.00	0.00	0.00	4.05
750	210	9450	0.05	0.00	0.00	0.00	3.87
750	240	10800	0.08	0.07	0.00	0.00	4.17

Table 34: Sugar mass after pretreatment (ultrasonic bath)

Power input (W)	**Mass (g)**					**Total sugars (g)**
	Mannose	**Fructose**	**Glucose**	**Xylose**	**Cellubiose**	
150	0.00	0.00	0.00	0.00	1.52	1.52
150	0.00	0.00	0.00	0.00	1.54	1.54
150	0.00	0.00	0.00	0.00	1.49	1.49
150	0.00	0.00	0.00	0.00	1.50	1.50
150	0.00	0.00	0.00	0.00	1.54	1.54
150	0.00	0.00	0.00	0.00	1.48	1.48
150	0.00	0.00	0.00	0.00	1.47	1.47
150	0.00	0.00	0.00	0.00	1.51	1.51
300	0.25	0.00	0.00	0.00	1.07	1.32
300	0.06	0.00	0.00	0.00	1.04	1.10
300	0.00	0.00	0.00	0.00	1.07	1.07
300	0.01	0.01	0.00	0.00	1.13	1.15
300	0.01	0.00	0.00	0.00	1.16	1.17
300	0.00	0.00	0.00	0.00	1.06	1.06
300	0.00	0.00	0.00	0.00	1.10	1.10
300	0.00	0.00	0.00	0.00	0.47	0.47
450	0.00	0.04	0.00	0.00	1.03	1.07
450	0.00	0.01	0.00	0.00	0.82	0.83
450	0.02	0.01	0.00	0.00	1.11	1.14
450	0.00	0.00	0.00	0.00	0.83	0.83
450	0.01	0.00	0.00	0.00	0.78	0.80
450	0.01	0.00	0.00	0.00	0.79	0.81
450	0.02	0.00	0.00	0.00	0.82	0.83
450	0.02	0.00	0.00	0.00	0.73	0.75
600	0.01	0.00	0.00	0.00	0.84	0.85
600	0.01	0.01	0.00	0.00	0.83	0.86
600	0.00	0.00	0.00	0.00	0.80	0.80
600	0.00	0.03	0.00	0.00	0.78	0.81
600	0.00	0.00	0.00	0.00	0.78	0.78
600	0.00	0.00	0.00	0.00	0.81	0.81
600	0.00	0.00	0.00	0.00	0.46	0.46
600	0.00	0.00	0.00	0.00	0.89	0.89
750	0.00	0.00	0.00	0.00	0.89	0.89
750	0.02	0.00	0.00	0.00	0.88	0.90
750	0.00	0.00	0.00	0.00	0.78	0.78
750	0.01	0.00	0.00	0.00	0.78	0.79
750	0.00	0.00	0.00	0.00	0.84	0.84
750	0.01	0.00	0.00	0.00	0.78	0.79
750	0.01	0.00	0.00	0.00	0.74	0.75
750	0.02	0.01	0.00	0.00	0.79	0.82

Table 35: Areas obtained during pretreatment (ultrasonic probe)

Amplitude	Time	Area				
		Mannose	Fructose	Glucose	Xylose	Cellubiose
5	10	0.00	0.00	0.00	0.00	79984.80
5	20	0.00	0.00	0.00	0.00	70733.85
5	30	850.58	0.00	0.00	0.00	73424.96
5	40	0.00	945.39	0.00	0.00	70868.29
5	50	698.45	0.00	0.00	0.00	69859.24
5	60	755.26	0.00	0.00	0.00	75208.17
10	10	0.00	0.00	0.00	0.00	71904.05
10	20	0.00	540.20	0.00	0.00	68824.88
10	30	2305.27	0.00	0.00	0.00	68155.85
10	40	496.43	0.00	0.00	0.00	72438.40
10	50	590.47	0.00	0.00	0.00	65833.62
10	60	0.00	590.33	0.00	0.00	75884.54
15	10	0.00	0.00	0.00	0.00	77774.80
15	20	0.00	556.95	0.00	0.00	74052.13
15	30	0.00	0.00	0.00	0.00	75776.30
15	40	0.00	0.00	0.00	0.00	72308.83
15	50	0.00	0.00	0.00	0.00	75383.62
15	60	0.00	1499.44	0.00	0.00	81297.82
20	10	0.00	0.00	0.00	0.00	81872.55
20	20	0.00	0.00	0.00	0.00	77823.00
20	30	0.00	0.00	0.00	0.00	80037.30
20	40	0.00	0.00	0.00	0.00	76516.26
20	50	0.00	0.00	0.00	0.00	73016.95
20	60	0.00	0.00	0.00	0.00	78679.31
25	10	0.00	0.00	0.00	0.00	75396.27
25	20	0.00	0.00	0.00	0.00	76515.07
25	30	0.00	0.00	0.00	0.00	82309.54
25	40	0.00	0.00	0.00	0.00	75006.78
25	50	0.00	663.22	0.00	0.00	73225.90
25	60	0.00	0.00	0.00	0.00	68289.19

Table 36: Sugar concentrations after pretreatment (ultrasonic probe)

Amplitude	Time	Concentration (g/L)				
		Mannose	Fructose	Glucose	Xylose	Cellubiose
5	10	0.00	0.00	0.00	0.00	4.46
5	20	0.00	0.00	0.00	0.00	3.94
5	30	0.07	0.00	0.00	0.00	4.09
5	40	0.00	0.10	0.00	0.00	3.95
5	50	0.06	0.00	0.00	0.00	3.89
5	60	0.07	0.00	0.00	0.00	4.19
10	10	0.00	0.00	0.00	0.00	4.01
10	20	0.00	0.06	0.00	0.00	3.84
10	30	0.20	0.00	0.00	0.00	3.80
10	40	0.04	0.00	0.00	0.00	4.04
10	50	0.05	0.00	0.00	0.00	3.67
10	60	0.00	0.06	0.00	0.00	4.23
15	10	0.00	0.00	0.00	0.00	4.34
15	20	0.00	0.06	0.00	0.00	4.13
15	30	0.00	0.00	0.00	0.00	4.22
15	40	0.00	0.00	0.00	0.00	4.03
15	50	0.00	0.00	0.00	0.00	4.20
15	60	0.00	0.15	0.00	0.00	4.53
20	10	0.00	0.00	0.00	0.00	4.56
20	20	0.00	0.00	0.00	0.00	4.34
20	30	0.00	0.00	0.00	0.00	4.46
20	40	0.00	0.00	0.00	0.00	4.27
20	50	0.00	0.00	0.00	0.00	4.07
20	60	0.00	0.00	0.00	0.00	4.39
25	10	0.00	0.00	0.00	0.00	4.20
25	20	0.00	0.00	0.00	0.00	4.27
25	30	0.00	0.00	0.00	0.00	4.59
25	40	0.00	0.00	0.00	0.00	4.18
25	50	0.00	0.07	0.00	0.00	4.08
25	60	0.00	0.00	0.00	0.00	3.81

Table 37: Sugar mass after pretreatment (ultrasonic bath)

Amplitude	**Time**	**Mass (g)**				
		Mannose	**Fructose**	**Glucose**	**Xylose**	**Cellubiose**
5	10	0.00	0.00	0.00	0.00	0.89
5	20	0.00	0.00	0.00	0.00	0.78
5	30	0.01	0.00	0.00	0.00	0.81
5	40	0.00	0.02	0.00	0.00	0.77
5	50	0.01	0.00	0.00	0.00	0.76
5	60	0.01	0.00	0.00	0.00	0.81
10	10	0.00	0.00	0.00	0.00	0.80
10	20	0.00	0.01	0.00	0.00	0.76
10	30	0.04	0.00	0.00	0.00	0.75
10	40	0.01	0.00	0.00	0.00	0.79
10	50	0.01	0.00	0.00	0.00	0.71
10	60	0.00	0.01	0.00	0.00	0.81
15	10	0.00	0.00	0.00	0.00	0.87
15	20	0.00	0.01	0.00	0.00	0.82
15	30	0.00	0.00	0.00	0.00	0.83
15	40	0.00	0.00	0.00	0.00	0.79
15	50	0.00	0.00	0.00	0.00	0.82
15	60	0.00	0.03	0.00	0.00	0.87
20	10	0.00	0.00	0.00	0.00	0.91
20	20	0.00	0.00	0.00	0.00	0.86
20	30	0.00	0.00	0.00	0.00	0.88
20	40	0.00	0.00	0.00	0.00	0.83
20	50	0.00	0.00	0.00	0.00	0.79
20	60	0.00	0.00	0.00	0.00	0.84
25	10	0.00	0.00	0.00	0.00	0.84
25	20	0.00	0.00	0.00	0.00	0.85
25	30	0.00	0.00	0.00	0.00	0.90
25	40	0.00	0.00	0.00	0.00	0.82
25	50	0.00	0.01	0.00	0.00	0.79
25	60	0.00	0.00	0.00	0.00	0.73

A.4 Thermochemical liquefaction experiments

Table 38: Liquefaction experiments done on the water hyacinth roots

Atmosphere	Liquefaction temperature (°C)	Wet biomass (g)	Dry biomass (g)	Bio-char yield (g)	Bio-char yield (wt%)
Nitrogen	240	100.2	8.2	4.0	49.1
	260	92.0	7.5	3.0	39.4
	280	100.3	8.2	3.2	39.0
	300	95.7	7.8	2.6	33.8
	320	103.1	8.4	2.3	27.1
	340	101.1	8.2	2.6	31.6
Carbon dioxide	240	99.2	8.1	4.1	51.2
	260	91.6	7.5	3.1	41.6
	280	100.5	8.2	3.2	39.5
	300	97.6	7.9	2.8	35.3
	340	98.9	8.0	3.5	44.0
Carbon monoxide	240	101.8	8.3	4.8	57.9
	260	105.6	8.6	3.6	41.9
	280	97.2	7.9	3.6	45.9
	300	100.3	8.2	3.6	44.5

Table 39: Liquefaction experiments done on the water hyacinth stems and leaves

Atmosphere	Liquefaction temperature (°C)	Wet biomass (g)	Dry biomass (g)	Bio-char yield (g)	Bio-char yield (wt%)
Nitrogen	240	50.1	11.4	5.2	45.7
	260	36.1	8.2	4.5	54.9
	280	50.2	11.4	5.4	47.4
	300	50.5	11.5	4.6	40.1
	320	50.4	11.4	3.7	32.3
	340	48.3	11.0	5.5	50.1
Carbon dioxide	280	50.5	11.5	4.3	37.7
	300	46.6	10.6	3.1	29.5
Carbon monoxide	240	53.6	12.2	6.0	49.3
	260	49.4	11.2	4.7	42.1

Table 40: Energy Dispersive X-ray Spectroscopy (EDS) results of water hyacinths

Component	**Atmosphere**	**Liquefaction temperature (°C)**	**Carbon (wt%)**	**Oxygen (wt%)**	**C/O**
Roots	N_2	240	45.34	54.66	0.83
		320	43.67	56.33	0.78
	CO_2	240	45.75	32.31	1.42
		300	44.15	32.92	1.34
	CO	240	45.55	44.53	1.02
		320	46.05	38.84	1.19
Stems and leaves	N_2	240	70.84	21.73	3.26
		300	75.27	19.89	3.78
	CO_2	300	67.34	32.66	2.06
	CO	240	55.51	44.49	1.25

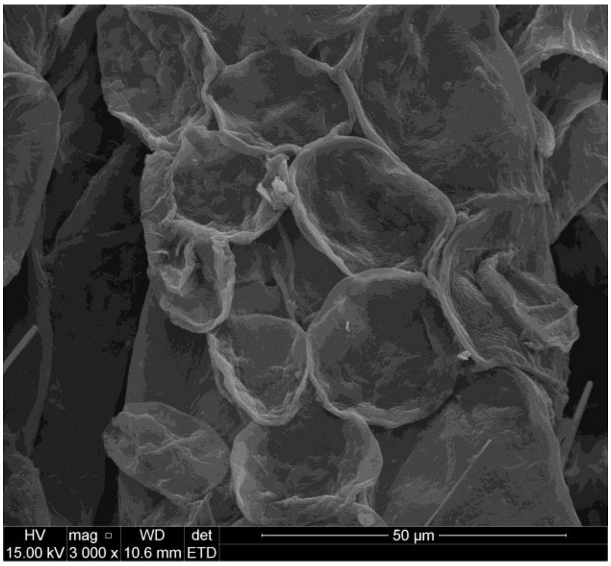

Figure 31: SEM image of raw feed (stems and leaves)

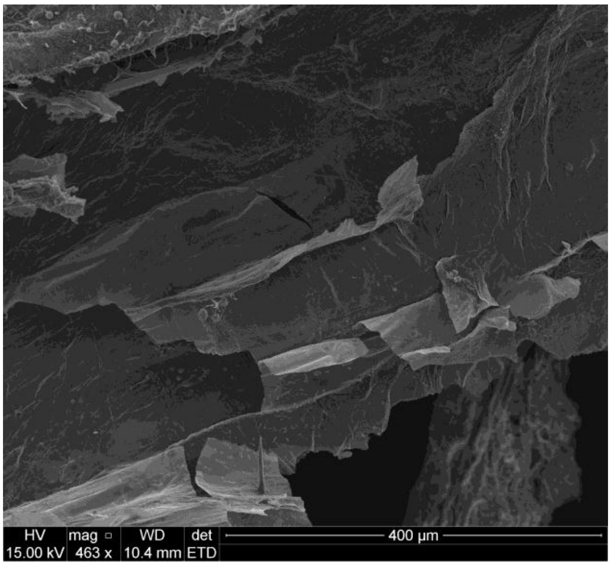

Figure 32: SEM image of raw feed (roots)

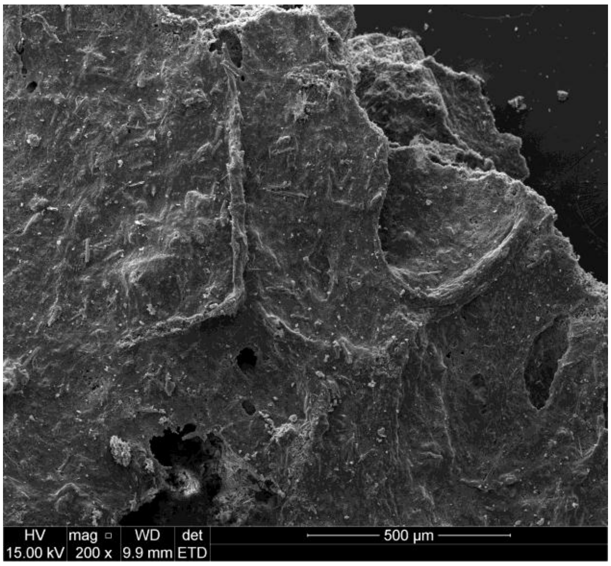

Figure 33: SEM image showing the effect of temperature on the extent of charring at 300°C (N_2, stems and leaves)

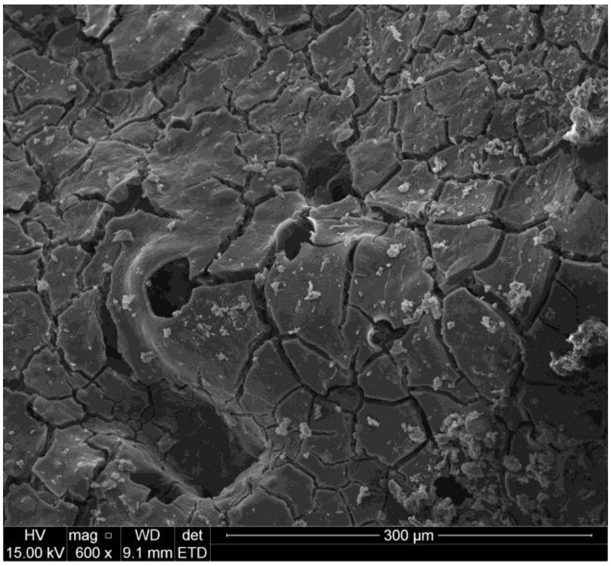

Figure 34: SEM image showing the effect of temperature on the extent of charring at 300°C (CO_2, stems and leaves)

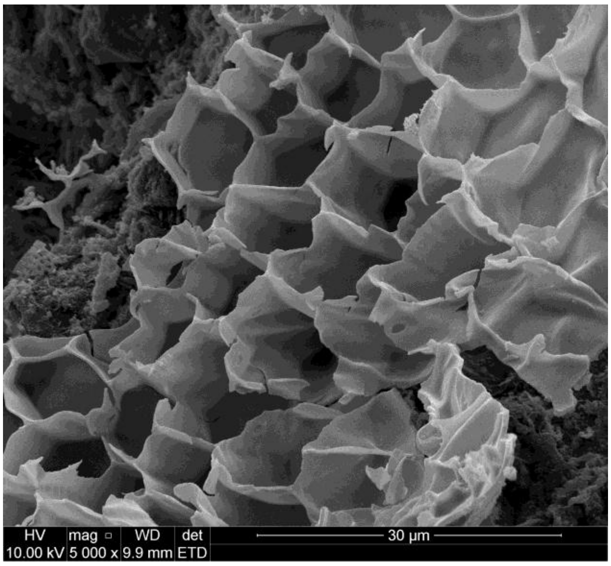

Figure 35: SEM image showing the effect of temperature on the extent of charring at 240°C (N_2, roots)

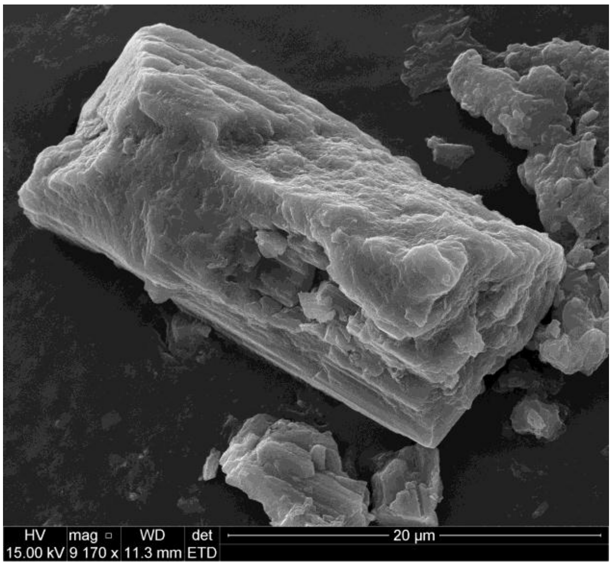

Figure 36: SEM image showing the effect of temperature on the extent of charring at 260°C (N_2, roots)

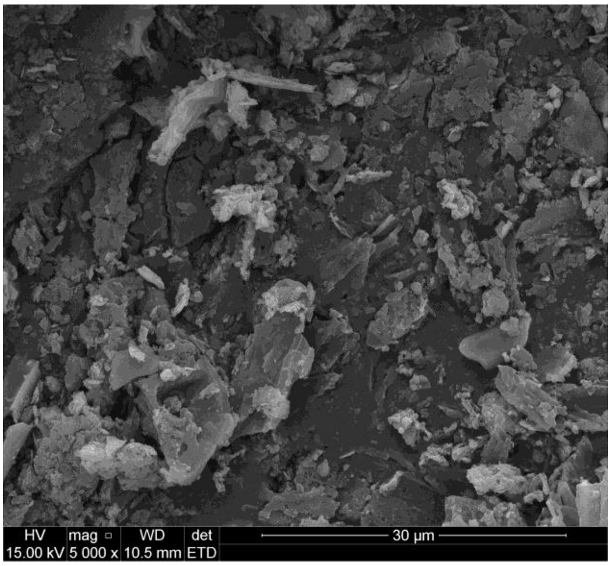

Figure 37: SEM image showing the effect of temperature on the extent of charring at 320°C (N_2, roots)

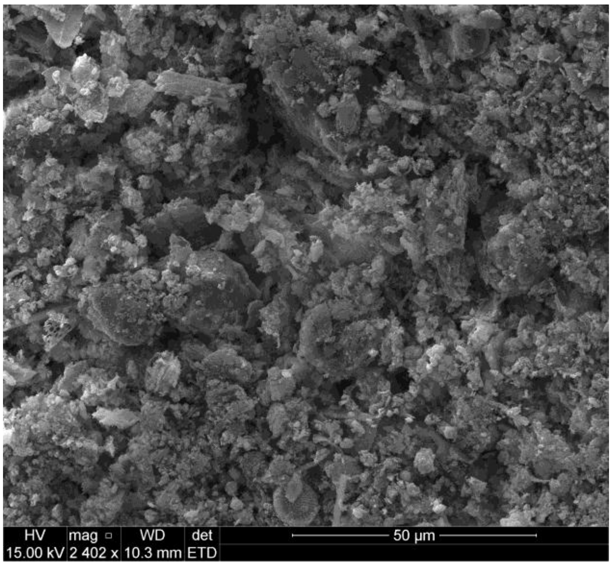

Figure 38: SEM image showing the effect of temperature on the extent of charring at 300°C (CO_2, roots)

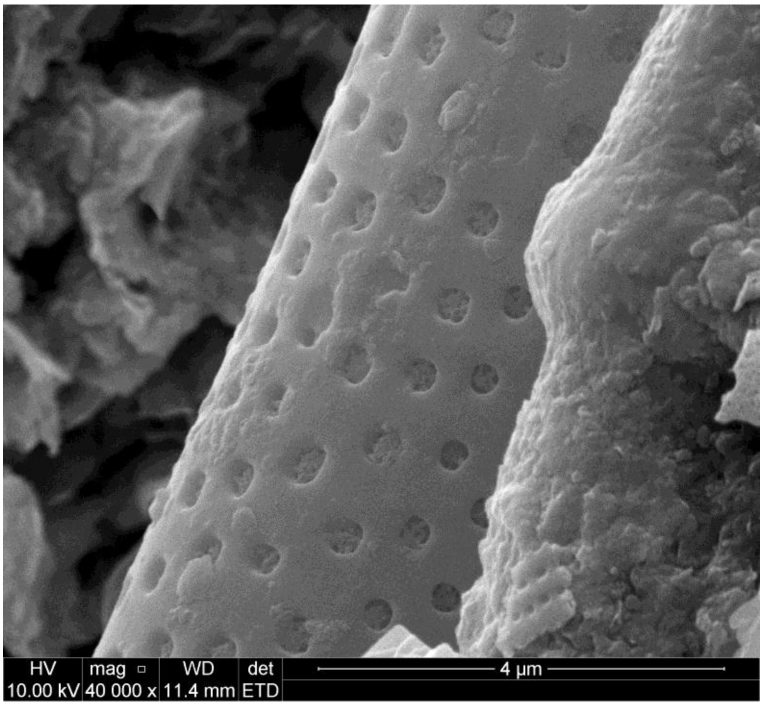

Figure 39: SEM image showing the effect of temperature on the extent of charring at 240°C (CO, roots)

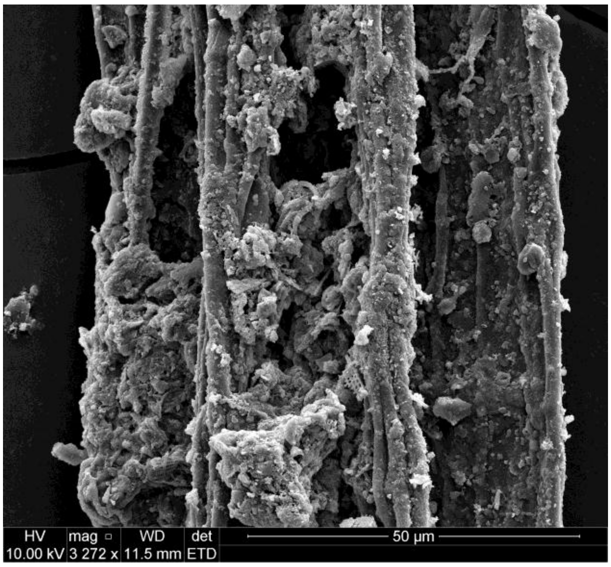

Figure 40: SEM image showing the effect of temperature on the extent of charring at 300°C (CO, roots)

A.5 Ethanol-gel experiments

Table 41: Burning time of ethanol-gel with different ethanol volume ratios

Ethanol concentration (vol%)	**Burning time (seconds)**			
	Test 1	**Test 2**	**Test 3**	**Average**
75	160	155	177	164
80	240	233	215	229
85	245	265	248	253
90	277	268	256	267
95	262	231	248	247

Table 42: Residue after burning the ethanol-gel

Ethanol concentration (vol%)	**Residue**				
	Test 1 (g)	**Test 2 (g)**	**Test 3 (g)**	**Average (g)**	**Average (wt%)**
75	2.4	2.4	2.3	2.4	47.0
80	2.0	2.0	2.0	2.0	40.3
85	1.9	2.0	2.0	2.0	39.5
90	1.3	1.8	1.7	1.6	32.3
95	1.8	1.8	1.8	1.8	35.8

Table 43: Higher heating values of ethanol-gel

Ethanol concentration (vol%)	**Higher heating value (MJ/kg)**
75	15.4
80	16.0
85	16.9
90	18.0
90	17.6
90	17.8
90	17.2
90	17.5
95	14.8