THERMOCHEMICAL LIQUEFACTION OF WATER HYACINTH

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ABSTRACT: The use of non-edible biomass should be investigated as alternatives for biofuel production. Aquatic weeds like water hyacinth (WH) are classified as third generation crops. WH in South Africa is an invasive species that brings forth many problems in the utilization of water resources. Liquefaction experiments were conducted on WH across a temperature range of 240 – 340ºC, at three different atmospheres. The maximum bio-char yield for the stem and leaves was found to be 54 ± 3.43wt% at temperature of 260ºC, and for the roots a maximum yield was obtained of 45.83± 3.2wt% at a temperature of 280ºC. Carbon monoxide was found to be the optimum atmosphere in liquefaction experiments of the roots, reaching on average a higher yield percentage of 4%. Due to low biomass loading in this investigation the production of bio-oil was found to be negligible. This investigation showed that it might be possible to use WH as feedstock for the production of renewable energy through thermochemical liquefaction. The calorific value (CV) was 10.887±0.451 MJ/kg and 23.306±0.451 MJ/kg for the roots and stem and leaves respectively. The high CV of the stem and leaves suggests that the possibility should be investigated for industrial application of the bio-char.

Keywords: biochar, biofuel, liquefaction

1 INTRODUCTION

Current estimations show that fossil fuel resources might be depleted within the next 120 years. This creates a great urgency to find renewable energy sources [1].

Biomass is defined as all living matter, in which solar energy is stored [1]. The energy in biomass is stored in chemical bonds. When this adjacent oxygen, hydrogen and carbon bonds are broken, by decomposition, combustion or digestion, the stored chemical energy is released [2]. This is done through biomass conversion processes namely: thermochemical conversion and biochemical conversion. The products formed in these conversion methods can further be used in the production of biofuels.

Liquefaction is a thermochemical conversion process. Liquefaction attempts to liquefy the feed without going through the gas phase. It entails heating the biomass in the presence of a catalyst under pressure. The process then yields a mixture of gas (between 2-10%), bio-char (between 5-40%) and oil (up to 40%) [3] This in return has many potential applications, including biopolymers and fuel or fuel additives [4].

Goyal *et al.* [1] further states the use of bio-oil, bio-char and bio-gas as follows: bio-oil can be used as a combustion fuel, bio-char can be used either as solids in boilers or for production of a hydrogen rich gas through thermal cracking, while bio-gas can be used as fuel for industrial combustion purposes [3].

Feedstock choices for biofuel production have brought up many a concern. In the past as the biomass requirements compete with edible crops for valuable land recourses [5]. Gressel [6] takes the argument of food versus fuel further. He states that using crops for biofuel production that is also set out for human consumption will have an effect on the prices of the feedstock. Larger demand for crop will also put strain on the environment which in return may influence the price of the feedstock as well as job cost.

In South Africa the biofuels strategy proposed to use sugar beets and sugar cane for bioethanol production, and sunflower, canola and soybean crops for the production of biodiesel [7].

The use of aquatic plants instead of terrestrial plants is seen as the next promising renewable energy resource. Aquatic plant species do not compete with food crops for arable land [8] and forms part of the third generation of biofuel crops.

Gressel [6] defines the different generation of biofuel crops as first, second and third generation crops. First generation crops include sugarcane, cereal grains and oilseeds, producing bioethanol, biobutanol and biodiesel respectively. The problem with first generation crops is the fact that these crops compete directly with food supply. Gressel [6] stated that in the United States 15 % more arable land was needed than available to supply the demand of biofuels. This led to the birth of second generation biofuel crops in which alternative crops or modified crops was investigated, which did not directly compete with food supply. These crops include castor beans, certain types of grasses and straws. Third generation crops are defined as micro-algae and cyanobacteria, which were initially found to have much higher yields than even the most effective conventional crops.

According to Nigam [9] water hyacinth (WH) is seen as a potential source of cellulose and hemicellulose for biomass conversion processes. In general WH is considered to be rich in hemicelluloses and contains virtually no lignin [5]. Ashwaty *et al.* [5] researched WH as a potential feedstock for bio-ethanol production and found that the biomass productivity is very high. It was further argued that WH is an aquatic weed and not a food crop. Furthermore it is abundantly available in certain parts of the world, making it a suitable feedstock. Another factor that plays a role is the growth rate of WH which is up to 100 t per ha per year.

Table I shows the composition of WH as reported in previous studies [9].

Table I: Average composition of WH

Constituents	wt% of wet WH
Total solids (TSs)	5 – 7.6
Moisture Content	92.8 – 95.0
Volatile solids (as % of TSs)	4.2 – 6.1
Organic compounds	% TSs
Hemicellulose	48.70 ± 0.027
Cellulose	18.20 ± 0.012
Lignin	3.50 ± 0.004
Crude protein	13.30 ± 0.020

Gressel [6] states that the advantages of an ideal energy crop for biofuel production is that it is, naturally grown, high cellulose and low lignin content per unit volume of dry matter, easily degradable, does not compete with arable crops for light, space and nutrients, and resists pests, insects and disease.

1.1 Previous liquefaction studies on WH

Table II shows previous results reported in literature for liquefaction of WH.

Table II: Liquefaction results of previous studies.

Reference	Temperature	wt% Yield
Bio-oil yield:		
Lu *et al* [10]	350 ° C	12.6
Elliot *et al* [11]	350 ° C	26.0
Bio-char yield:		
Lu *et al* [10]	300 ° C	48.9

The results shown in Table II for the bio-oil, is not within the range of liquefaction temperatures [4] and hydrodeoxygenation reactions start to take place at these temperatures.

1.2 Influence of temperature on thermochemical liquefaction

Studies [12, 13, 14] have shown that an increase in temperature increases the bio-oil yield and that the opposite is true in the case of the production of bio-char. The increased yield of bio-oil is explained by the observation that higher temperatures assist in the separation of the oily and aqueous phases [12].

1.3 The influence of reaction atmosphere on thermochemical liquefaction

The reaction atmosphere has an influence on the reaction pathway followed in the production of the bio-oil and bio-char [15]. According to Barnard [16] the use of a reduction gas favours the abstraction process, whereas the absence of a reduction gas favours pyrolytic evolution. Barnard [16] also mentioned that the atmosphere required for the liquefaction process is dependent on the hydrogen content of the biomass due to the internal hydrogen shuttling that occurs in some cases.

1.4 Calorific value (CV)

Table III: Reported calorific values for bio-char and coal

Feedstock	CV – (MJ/kg)
Bio-char	
Palm oil [17]	22 - 26
Sunflower husk [18]	23.51
Soy cake [18]	22.78
Sugarbeet bagasse [18]	24.52
Peanut shells [18]	20.36
Coal [19]	
Hard coal	23.9
Brown coal	17.4 – 23.9
Lignite	<17.4

From Table III it is suggested that bio-char can be used as a solid biofuel.

2 MATERIALS AND METHODS

2.1 Materials

WH was harvested from the Vaal River specifically in the north-west of the Free State province of South Africa. After harvesting the feedstock, the roots were separated from the stem and leaves, this was then used as two different feedstock.

The roots were cut into smaller pieces by hand, and rinse before use. The stem and leaves were made fine mechanically with the use of a blender. Some of the moisture was removed by means of chemical extraction.

The chemical extraction entailed the use of three chemicals namely two enzymes Celluclast and Pectinex Ultra SP-L and a surfactant Tween 80. The biomass loading was 23% for the stems and leaves.

Table IV: Constituents of stems and leaves

Constituents	wt% WH (wet base)
Ash	2.10
Moisture content	85.44
Protein	1.89
Fat	0.21
Neutral detergent fibre	7.88
Acid detergent fibre	3.41
Acid detergent lignin	0.32
Carbohydrates	9.68

Table V: Constituents of roots

Constituents	wt% WH (wet base)
Ash	2.63
Moisture Content	90.56
Protein	0.21
Fat	0.08
Neutral detergent fibre	3.73
Acid detergent fibre	1.39
Acid detergent lignin	0.62
Carbohydrates	5.57

From Table IV and Table V it can be seen that the feedstocks have very high moisture content and low lignin content. The low lignin content is expected to be beneficial for liquefaction [7].

The investigation entailed using the moisture contained in the feedstock as solvent for the process.

Table VI shows the carbon to oxygen ratio of the raw feedstock.

Table VI: Carbon to Oxygen ratio of raw feedstock.

Feedstock	C/O
Stem and leaves	1.06
Roots	0.78

2.2 Chemicals

Different atmospheres were investigated in this study, namely nitrogen, carbon monoxide and carbon dioxide. This was done in order to see the effect of different atmospheres on the final product yields of liquefaction as well as the influence on the carbon to oxygen ratio of the products.

2.3 Experimental procedure

The experimental procedure was identical for both feedstocks. An initial amount of biomass was weighed off. For the roots 100 g were used and for the stem and leaves 50 g for each experiment. The biomass was then loaded into an autoclave, with a similar experimental setup as reported in literature [9].

The autoclave was closed and bolted shut with screw caps after which it was torqued to 70 N.m. The setup was then purged and pressurised. Initially the autoclave was pressurised with Ultra High Purity (UHP) nitrogen to 20 bar. This was repeated five times to purge the system.

The autoclave was then pressurized with the applicable atmosphere to 10 bar. A heating jacket was connected to the autoclave, the magnetic stirrer switch on and the run started.

The autoclave was heated at an average rate of 2.92 K/min for each experiment. The residence time inside the autoclave was kept constant at 30 min. For this time the internal temperature was also kept constant with a temperature controller.

The temperature dependent experiments were done with nitrogen as atmosphere for both the feedstocks, and over a range of six temperatures, namely 240 – 340 °C with intervals of 20 °C.

The atmosphere dependent experiments were done with carbon monoxide, nitrogen and carbon dioxide as atmosphere.

After the liquefaction process was completed and the reactors 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 ºC.

2.4 Analytical method

The raw feed was sent to the Agricultural Research Council (ARC) for characterisation of the feedstock. 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.

For the SEM and EDS analysis the samples were coated with gold as well as palladium under a vacuum before investigation under the microscope. The raw biomass as well as the bio-char was dried over night at 105 ºC before the analysis.

The calorific value (CV) of the bio-char was determined with a bombcalorie meter.

3 RESULTS AND DISCUSSION

3.1 Temperature

The bio-char percentage yield is shown in figure 1

Figure 2 shows the effect of temperature on the bio-char yield for both feedstocks with nitrogen as atmosphere.

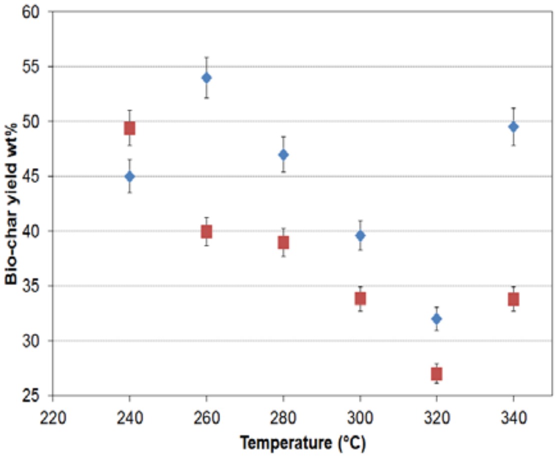
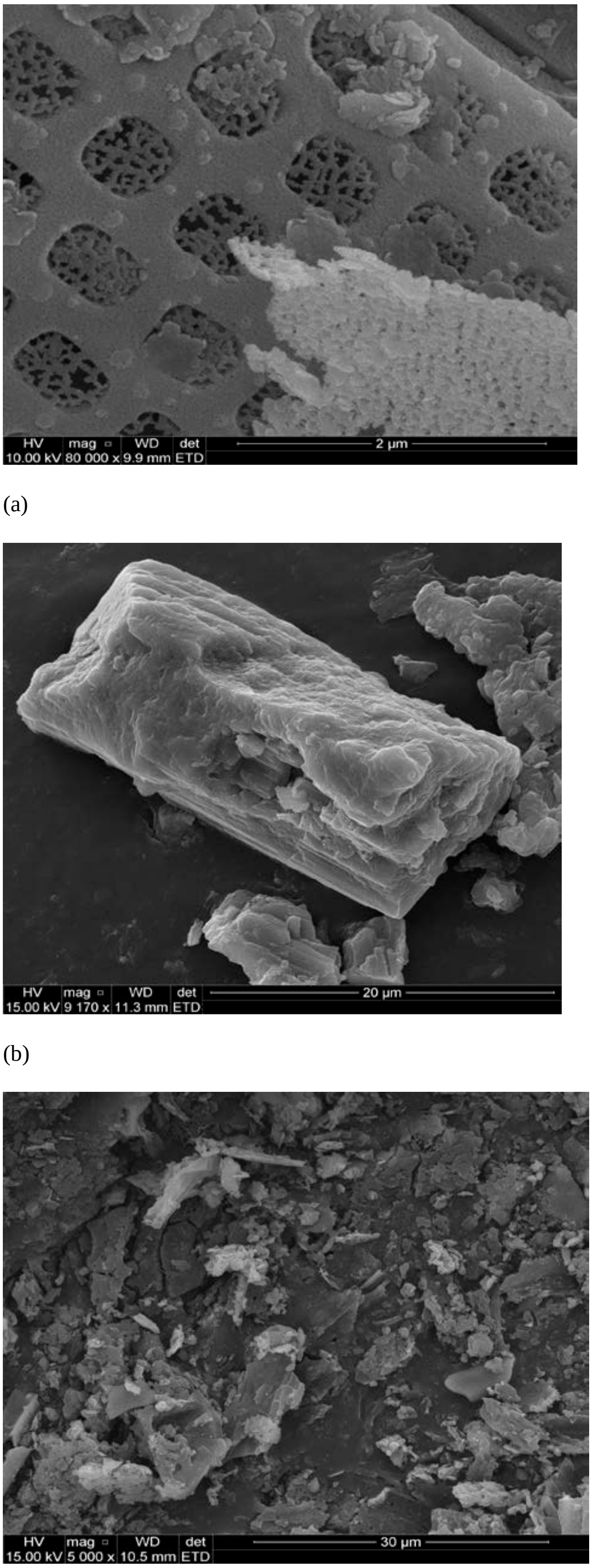


Figure 1: Effect of temperature on bio-char yield during thermochemical liquefaction (■ Roots, ◆ stem and leaves)

For the stems and leaves an optimum yield of 54±3.43 wt% is reached at 260 °C. An optimum yield for the roots of 49±3.2 wt% is reached at 240 °C. The effect of temperature is clearly shown in Figure 1, the decline in yield at higher temperatures can be explained by the fact that at higher temperatures volatile components comes off thus giving a lower percentage yield of the solid residue. As stated in the introduction, higher temperatures favour oil-yields, and above 300 ºC it has also been reported that hydrocracking does start to occur [12].

The increase at 340ºC is found to be inconsistent with the results although this temperature is not in the liquefaction range anymore and is technically classified as pyrolysis [7]. A possible explanation for the higher yield might be that different compounds formed in the pyrolysis process might settle around the biomass, like waxes and oils.

Further investigation showed that at 240ºC the biomass is not completely charred this is shown in Figure 2.



(a)

(b)

(c)

Figure 2: Effect of temperature degree of charring that occurs at different temperatures ((a) 240ºC, (b) 260ºC, (c) 320ºC)

The SEM photos shown in Figure 2 were taken of the roots at 240ºC, 260ºC and 320ºC respectively with nitrogen as reaction atmosphere.

From Figure 2 (a) it can be seen that the cell structure although partially damaged is still present. In Figure 2 (b) it is seen that no noticeable plant structure is left. In Figure 2 (c) it is clear that the charring process is fully completed.

Thus the optimum yield for the roots can be assumed to be at 260 ºC, disregarding the yield at 240 ºC due to incomplete charring.

The temperature effect on the carbon to oxygen ratio is shown in Table VII.

Table VII: Carbon to oxygen ratio with nitrogen as atmosphere at different temperatures.

	Temperature (ºC)	C/O
Stem and leaves:		
	240	3.26
	300	3.78
Roots:		
	240	
	320	1.59

From Table VII it can be seen that there is a slight increase in the ratio, this can again be explained by the different reaction paths followed at higher temperatures, with the volatile components starting to come off. It is noted that with an increase in temperature the oxygen percentage decreases slightly.

It should also be noted that the ratio of the stems and leaves are much higher than that of the roots.

3.2 Different atmospheres

The effect of the use of different atmospheres is shown for the roots in Figure 3.

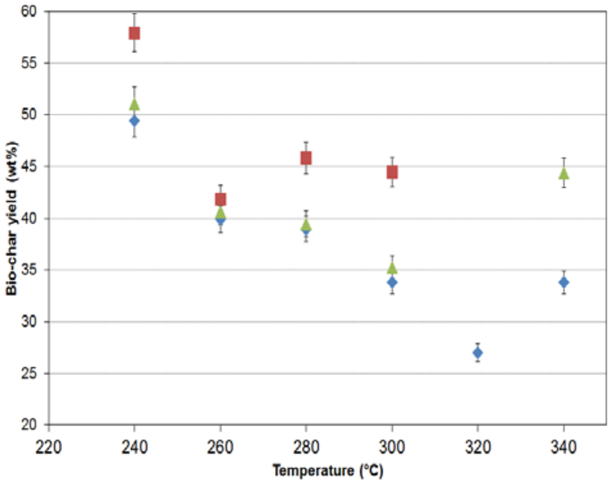


Figure 3: Effect of different atmospheres on bio-char yield (🟥 carbon monoxide, ◆ nitrogen, ▲carbon dioxide)

From Figure 3 it can be seen that the highest yield is obtained with carbon dioxide as atmosphere for the roots. The temperature where the highest yield was obtained stayed constant at 260 ºC although for carbon monoxide the optimum yield was obtained at 280 ºC.

Carbon monoxide is not a reducing gas this indicates that the hydrogen content of the feedstock might be high.

Table VIII show the different percentage yields at the different atmospheres.

Table VIII: Bio-char yield of the roots at different atmospheres.

	Temperature (ºC)	Bio-char yield (%wt)
Roots:		
Carbon Monoxide	280	45.83±3.2
Nitrogen	260	39.93 ± 3.2
Carbon dioxide	260	40.68 ± 3.2

From Table VII it can be seen that carbon monoxide gave the highest yield, whereas carbon dioxide and nitrogen virtually stayed the same. Nitrogen is only an inert gas and would thus be the baseline for these experiments.

For the stem and leaves opposite data was found with the optimum reaction atmosphere as nitrogen giving a bio-char yield of 54 ± 3.43wt%, at the optimum temperature. For carbon monoxide the yield was found to as 45.2 ± 3.43wt%, it was also found that at 240 ºC the carbon monoxide yield was significantly lower. The same results were found for the carbon dioxide. Thus making nitrogen the optimum gas for liquefaction of the stem and leaves. This might be indicative of low hydrogen content in the raw biomass, seeing as both the carbon monoxide and carbon dioxide are non-reducing gasses. In the absence of a reducing gas a lower yield means that low hydrogen shutting will occurred. It would thus be recommended to further investigate the yields at a different reducing atmosphere like hydrogen.

Table IX shows the effect of different atmospheres on the carbon to oxygen ratio of the bio-char.

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

	Temperature (ºC)	C/O
Roots:		
Carbon Monoxide		
	240	1.02
	320	1.19
Nitrogen		
	240	0.82
	320	1.59
Carbon dioxide		
	240	1.42
	260	1.34

From Table IX it is seen that the C/O ratio is lower for the carbon monoxide. This is due to a much higher percentage of oxygen present in the bio-char. This percentage at 240 ºC is 27%, 32% and 44 % respectively for the nitrogen, carbon dioxide and the carbon monoxide.

The higher oxygen percentage present might also be an indication why a higher bio-char yield is obtained.

3.3 Calorific value (CV) of the bio-char

The CV value of the bio-char was determined to be 10.887±0.451 MJ/kg for the roots and 23.306±0.451 MJ/kg for the stem and leaves. The CV of the roots are low, in comparison to the stem and leaves. This can be explained by the fact that the nature of the plant is to extract heavy metals from water. Thus certain impurities are still contained in the roots. Some traces of sand and gravel were found to still be present in the bio-char this was noted during SEM analysis.

The CV of the stems and leaves are high. It is within the range of CV for coal which suggest that the bio-char can be used as solid bio-fuel in industrial processes.

3.4 Bio-oil yield

Due to the low biomass loading the bio-oil yield was found to be negligible. The biomass loading was kept constant at 8% and 23% respectively for the roots and the stem and leaves.

Extraction chemicals, namely acetone and chloroform, were investigated to see if it would be possible to extract bio-oil. This was found ineffective when the liquid obtained from liquefaction was put in a Rotavaporater.

4 CONCLUSIONS

The optimum temperature for bio-char production was found to be 260ºC with nitrogen and carbon dioxide as atmosphere and 280ºC for carbon monoxide. The maximum bio-char yield for the roots was found to be 45.83±3.2wt%. While for the stem and leaves the yield was found to be 54 ± 3.43 wt%.

Carbon monoxide was found to be the optimum atmosphere for liquefaction of the roots. This conclusion is drawn from the fact that the overall percentage yield was higher than that for the other two atmospheres.

It is recommended to further investigate the composition of the bio-char. Compositional analysis will conclude on the possibility of using the bio-char as solid fuel in industrial applications. Further compositional analysis would also explain the liquefaction reaction path for WH better, and give light to inconsistencies encountered in this investigation.

This investigation did however show that the successful liquefaction of WH is possible, and products obtained can be used as solid fuel.

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