

**Effect of Temperature on Oil Quality Obtained through Pyrolysis of Sugarcane Bagasse**

Author

Stegen, Sascha

Published

2018-03

Thesis Type

Thesis (Masters)

School

School of Eng & Built Env

DOI

[10.25904/1912/1063](https://doi.org/10.25904/1912/1063)

Rights statement

The author owns the copyright in this thesis, unless stated otherwise.

Downloaded from

<http://hdl.handle.net/10072/376521>

Griffith Research Online

<https://research-repository.griffith.edu.au>



# Effect of Temperature on Oil Quality Obtained through Pyrolysis of Sugarcane Bagasse

Sascha Stegen

Griffith University  
School of Engineering

A thesis submitted in fulfilment of the requirements of the degree of

**Master of Philosophy**

March 2018



## ***Abstract***

In the last few centuries the world-wide energy demand rose to a stage where traditional power-supply networks struggle to satisfy the necessary supply of energy. Consequently, humanity is still largely dependent on every energy source possible and primarily environmentally unfriendly sources such as coal, fossil-oils, nuclear etc. Governments world-wide finally realised that those recourses are limited and began to subsidise renewable energy solutions such as solar and wind energy, but by neglecting the fact that those sources have problems to supply energy 24/7 to the customers. Pyrolysis from bio feedstock is one of the technologies which can not only produce oil and gas for generators as well as fertiliser, but also conquer another problem arising from modern society, garbage reduction. Pyrolysis does exist for many years now, but the technology has not often been employed due to high initial investments, maintenance, and other factors. Furthermore, most of the conducted pyrolysis laboratory experiments also focused on expensive setups, catalysts etc., which create potentially good results, but consequently the pyrolysis process continued of being unaffordable for private consumers and especially for smaller businesses, such as farmers. Several research projects focussed on the yield output, rather than the quality of the oil which could be used for power generation. As a result, the usage of the oil was not suitable for generators or even for storing, due to impurities as well as due to forming of aromatics which occur very often in the aim of maximising the yield output and causes wax deposits, which can cause severe damage in machines operated with fuel produced from this oil.

In this research pyrolysis experiments were conducted with the focus on increasing the oil quality by changing the temperature parameters, with a setup which is as simple as possible in order to make the setup mainstream capable, but also with the possibility of upscaling in mind. Although there are numerous feedstocks to choose from, sugarcane bagasse was chosen to be the feedstock of this research. This feedstock appears to be ideal, as the consumption and therefore the sugarcane bagasse waste rose significantly in the last century. At first the simplistic test rig was designed to determine the most suitable heating ramps and finally to investigate maximum temperatures from 300°C up to 650°C, based on the literature review conducted. This returned an overall picture at

what temperature the best possible oil output for this feedstock and simplistic set-up can be. After analysis of the different oil outputs, the temperature range was more refined and the ramp, which proved to be the best, was fixed. The final analysis is conducted in a narrowed temperature band of 450°C to 550°C and showed very promising results at 550°C not only in regard of a 11% increase of the higher heating value, which would mean that if a person consumes an average of 800kwh per year and everybody on this planet would use pyrolysis as a primary energy source, 38 million tonnes less of feedstock would be needed per year world-wide. Furthermore, storage capabilities of oil produced by 550°C showed an immense storage capability improvement, due to a very low amount of aromatics in comparison to temperatures above and below 550°C. Furthermore, the analysis was repeated four months after the experiments to observe any build-up of wax deposits from possible aromatics. The results were found to be exactly the same in regard to the HHV as well as the FTIR spectra of oil. Overall the research project proved that pyrolysis can be affordable, but also can produce good quality oil at the same time. Consequently, pyrolysis can play a vital role in the run for sustainable energy resources in the future.

## Statement of Originality

*This work has not previously been submitted for a degree or diploma in any university. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made in the thesis itself.*

Sascha Stegen



# TABLE OF CONTENTS

<b>1</b>	<b>INTRODUCTION .....</b>	<b>1</b>
1.1	Aim and Objectives .....	4
<b>2</b>	<b>LITERATURE REVIEW .....</b>	<b>5</b>
2.1.1	Significance of research project in regard to the Australian waste management.....	6
2.1.2	Significance of research project in regard to energy production .....	8
<b>2.2</b>	<b>Biomass Theory and Pyrolysis Output .....</b>	<b>10</b>
2.2.1	Sugarcane Bagasse.....	10
2.2.2	Composition of Biomass.....	11
<b>2.3</b>	<b>Biomass to bioenergy technologies .....</b>	<b>13</b>
2.3.1	Biochemical Process.....	14
2.3.2	Thermochemical Process .....	15
<b>2.4</b>	<b>The Pyrolysis Process .....</b>	<b>19</b>
2.4.1	Factors affecting the pyrolysis output.....	22
2.4.1.1	Oil Output .....	23
2.4.2	Traditional (Slow) Pyrolysis .....	24
2.4.3	Fast and Flash Pyrolysis .....	25
2.4.4	Reactor Types .....	25
2.4.4.1	Fixed bed reactor .....	26
2.4.4.2	Fluidized bed .....	26
2.4.4.3	Rotating cone pyrolyzer.....	27
2.4.4.4	Ablative pyrolysis reactor.....	28
2.4.4.5	Vacuum pyrolysis .....	28
2.4.4.6	Auger reactor .....	28
2.4.5	Different heating methods for Pyrolysis.....	29
2.4.6	Other Pyrolysis output considerations .....	32
2.4.6.1	Storage Stability Problem of Pyrolysis Bio-Fuel.....	32
2.4.7	Upgrading of Pyrolysis Bio-Oil Output.....	34
<b>2.5</b>	<b>Measurement methods of Oil output .....</b>	<b>37</b>
2.5.1	Calorific value .....	38
2.5.2	Viscosity .....	39
2.5.3	pH measurements.....	40
2.5.4	FTIR and GC-MS .....	41
<b>3</b>	<b>METHODOLOGY .....</b>	<b>43</b>
<b>3.1</b>	<b>Feedstock.....</b>	<b>43</b>
<b>3.2</b>	<b>Pyrolysis Test Rig .....</b>	<b>43</b>
3.2.1	Reactor design .....	44

3.3	<b>Reactor Operation .....</b>	<b>49</b>
3.4	<b>Analyses .....</b>	<b>50</b>
3.4.1	Mass Balance .....	52
3.4.2	Energy balance.....	52
<b>4</b>	<b>RESULTS AND DISCUSSION .....</b>	<b>53</b>
4.1	<b>Effect of pyrolysis temperature (300°C to 600°C) on chemical composition of sugarcane bagasse .....</b>	<b>53</b>
4.1.1	Effect of temperature range of 450 °C to 550 °C on bio-oil quality.....	57
4.2	<b>Further Concept Work .....</b>	<b>63</b>
4.2.1	Stainless steel reactor design concept.....	63
4.2.2	Choosing of a potential catalyst.....	64
<b>5</b>	<b>CONCLUSION.....</b>	<b>65</b>
<b>6</b>	<b>FUTURE WORK.....</b>	<b>66</b>
<b>7</b>	<b>REFERENCES AND APPENDICES .....</b>	<b>67</b>
	References .....	67
<b>8</b>	<b>APPENDICES .....</b>	<b>77</b>
8.1	<b>Oil Composition Based on Feedstock.....</b>	<b>77</b>
8.2	<b>Bio Oil Composition Limits .....</b>	<b>79</b>
8.3	<b>Analysis legends and tables.....</b>	<b>81</b>



## List of tables

TABLE 1: FEEDSTOCK COMPOSITION [59].....	12
TABLE 2: FEEDSTOCK COMPARISON FOR FAST PYROLYSIS PROCESS (ELEMENTAL ANALYSIS IS ON A DRY WEIGHT BASIS (DB)) [4, 63, 64] .....	13
TABLE 3: MAIN PRODUCTION METHODS OF METHANOL AND BIO-METHANOL [66] .....	14
TABLE 4: PYROLYSIS TYPE COMPARISON [72, 83, 84] .....	20
TABLE 5: TYPICAL BIO-OIL COMPOSITION OF BIO CRUDE OIL [95] .....	23
TABLE 6: API AND DENSITY COMPARISON BETWEEN BITUMEN AND LIGHT OIL .....	40
TABLE 7: REACTOR PARAMETERS OF MAXIMUM TEMPERATURE, HEATING RATE AND CALCULATED TIME UNTIL MAXIMUM TEMPERATURE IS REACHED .....	48
TABLE 8: CHEMICAL COMPOSITION OF THE SUGARCANE BAGASSE .....	53
TABLE 9: ELEMENTAL COMPOSITION, C/H, C/O AND CALORIFIC HEATING VALUE (MF BASIS) OF BIOCHAR AND OIL OBTAINED DURING PYROLYSIS OF SUGARCANE AT 300-600 °C. ....	55
TABLE 10: MASS BALANCE AVERAGE OF SUGARCANE BAGASSE PYROLYSIS.....	56
TABLE 11: ELEMENTAL COMPOSITION, C/H, C/O AND CALORIFIC HEATING VALUE (MF BASIS) OF BIO-OIL OBTAINED DURING PYROLYSIS OF SUGARCANE AT 450-550 °C .....	58
TABLE 12: COMPOSITION ANALYSIS OF SOLID OUTPUT FOR NARROWED DOWN TEMPERATURE RANGE .....	60
TABLE 13: MASS BALANCE AVERAGE OF SUGARCANE BAGASSE PYROLYSIS.....	61
TABLE 14: ENERGY BALANCE FOR THE PYROLYSIS PROCESS AT THE STUDIED TEMPERATURES BASED ON THE OIL HHV.....	62
TABLE 15: PERCENTAGE OF HYDROGEN OF BIO OIL DERIVED FROM THE PYROLYSIS PROCESS [63] .....	77
TABLE 16: BIO OIL COMPOSITION .....	79

# List of figures

FIGURE 1: WORLD ENERGY DEMAND FORECAST [34] .....	5
FIGURE 2: RATE OF AUSTRALIAN WASTE GENERATION COMPARED TO GROSS VALUE ADDED (GVA) AND POPULATION GROWTH. FROM 1997 TO 2012 [39] .....	6
FIGURE 3: WASTE MANAGEMENT BY MATERIAL (% OF MATERIAL TOTAL GENERATION) 2009-10 [39] .....	7
FIGURE 4: AUSTRALIAN INTERNATIONAL TRADE OF WASTE [39] .....	7
FIGURE 5: WORLD SUGAR CONSUMPTION [41] .....	8
FIGURE 6: PROCESS FLOW SHEET FOR BIOCHEMICAL CONVERSION WITH HYDROLYSIS AND FERMENTATION [71] .....	15
FIGURE 7: THERMAL CONVERSION TECHNOLOGIES.....	16
FIGURE 8: PROCESS FLOWSHEET FOR THERMOCHEMICAL CONVERSION WITH GASIFICATION AND SYNTHESIS [71] .....	17
FIGURE 9: PROCESS FLOWSHEET FOR THERMOCHEMICAL CONVERSION WITH GASIFICATION AND SYNGAS FERMENTATION [71] .....	17
FIGURE 10: USAGE OF PYROLYSIS BIO-OILS [81] .....	18
FIGURE 11: COMMON PYROLYSIS PROCESS.....	19
FIGURE 12: OUTPUT EXAMPLE OF PYROLYSIS METHOD [86] .....	21
FIGURE 13: PYROLYSIS TEST RIG .....	21
FIGURE 14: FLUIDIZED-BED REACTOR [110] .....	27
FIGURE 15: CROSS SECTION OF THE ROTATING CONE REACTOR [111] .....	27
FIGURE 16: PELTIER ELEMENT [38].....	30
FIGURE 17: LINEAR SOLAR PYROLYSIS REACTOR SETUP [119] .....	31
FIGURE 18: AGING OF BIO-OILS AT DIFFERENT TEMPERATURES [94] .....	33
FIGURE 19: BIO-OIL USAGE DIRECTLY IN DIESEL ENGINES [106] .....	34
FIGURE 20: BIO-OIL GASIFICATION [106] .....	35
FIGURE 21: BIO-OIL FERMENTATION [106] .....	35
FIGURE 22: BIO-OIL HYDROCRACKING [106] .....	36
FIGURE 23: DSC MEASUREMENT METHOD [122].....	39
FIGURE 24: CALORIFIC BOMB [123] .....	39
FIGURE 25: FTIR GRAPH EXAMPLE [127] .....	41
FIGURE 26: FTIR MEASUREMENT METHOD [127] .....	41
FIGURE 27: GC-MS SETUP [129] .....	42
FIGURE 28: EXPERIMENTAL SET-UP SHOWING THE GLASS PYROLYSIS REACTOR, ELECTRIC HEATING SYSTEM, CONDENSATION TRAIN, GAS SAMPLING, OIL COLLECTION AND VACUUM COOLING SYSTEM.....	50
FIGURE 29: FTIR SPECTRA OF OIL OBTAINED DURING THE PYROLYSIS OF SUGARCANE BAGASSE AT A) 300 °C, B) 400 °C, C) 500 °C, AND D) 600 °C.....	57
FIGURE 30: FTIR SPECTRA OF OIL OBTAINED DURING THE PYROLYSIS OF SUGARCANE BAGASSE: A) REFERENCE CURVE FROM WORST PREVIOUS SAMPLE, B) 450 °C, C) 500 °C, AND D) 550 °C .....	59
FIGURE 31: STEEL REACTOR CONCEPT SET-UP .....	63
FIGURE 32: STEEL REACTOR TUBE INLET .....	64

## Abbreviations Used in this Thesis

ASTM	- American Society for Testing and Materials
(TAN)	
Solvent	- Titration Solvent
°C	- Centi degrees Celsius
API	- American Petroleum Institute
ATR	- Attenuated Total Reflectance
AU\$	- Australian Dollar
C	- Carbon Emission
db	- dry weight basis
DSC	- Differential Scanning Calorimetry
DTA	- Differential Thermal Analysis
EF	- Emission Factor
FTIR	- Fourier-Transform Infrared Spectroscopy
GC-MS	- Gas Chromatography – Mass Spectrometry
GHG	- Greenhouse gas
HHV	- Higher Heating Value
	Inductively Coupled Plasma-Optical Emission
ICP-OES	- Spectroscopy
J	- Joules
K	- Kelvin
KBr	- Potassium bromide
kg	- Kilogram
kWh	- kilo Watt hours
NREL	- National Renewable Energy Laboratory
PCB	- Printed Circuit Board
s	- Second
TAN	- Total Acid Number
TBN	- Total Base Number
TGA	- Thermogravimetry
TMA	- Thermomechanical Analysis dimensions
Y	- Yield
ZSM	- Hydrocarbon Zeolite Socony Mobil

## *Acknowledgements*

I would like to thank my principal supervisor Dr Prasad Kaparaju for the chance to complete my research project. The amount of experience and knowledge he has provided me with was immeasurable and I am very thankful for all the valuable input. His constant support deserves my utmost respect and gratitude.

I would like to thank my other principal supervisor Dr Sunil Herat, for his direction, his critical review of my work, and his continuous support, guidance, and encouragement which enabled me to work on this project.

Furthermore, I would also like to thank all my colleagues and friends at Griffith University who offered me help and support on countless occasions. My special thanks also to Dr Lalehvasht Moghaddam and Professor Bill Doherty, from the Centre for Tropical Crops and Bio commodities at the Queensland University of Technology for supporting my work and help with analysing the outputs, without this I would not have been able to progress in this project.

I also want to thank my parents, Elvira and Helmut Stegen, my sister Nicole Grauer and my brother-in-law Jürgen Grauer for all their support as well as my friends in Germany and Australia. Without them, I would not be who and where I am today.



# 1 Introduction

The major global concern on the depletion of fossil fuels and the increase in greenhouse gas emissions have given rise for research in alternative and clean fuels. Among the various renewable energy resources, biomass is considered as unique resource as it provides CO<sub>2</sub>-neutral renewable energy and surpasses many other renewable energy sources in terms of its abundance, energy value and versatility. Bioenergy accounts for almost 33% in the global energy mix [1]. In Australia, it is estimated that 50 million tonnes of biomass and organic waste are generated every year [2]. Use of biomass as potential feedstock for bio-energy production has significant environmental and economic benefits [3]. It not only reduces Australia's dependence on fossil fuel and carbon footprint but can also contribute to greening the economy by creating jobs in clean technologies [3]. However, the use of biomass resources for energy production is under-utilised [2, 4]. Furthermore, the disposal of these products creates substantial environmental and economic burdens.

Sugar industry is the second largest agro-industry in Australia with an annual revenue of \$1.2 billion in export sales and employs thousands of people in Queensland, Australia [5]. However, the collection and disposal of the sugarcane industry wastes poses significant challenge to the sustainable growth of the industry [6]. Previous studies have shown that agricultural waste may increase soil hydrophobicity and decrease water retention and infiltration rates [7], which creates dead soil [8]. Therefore, there is a shift in many oil producing countries towards more sustainable methods of disposal [9].

In Australia approximately 10 million tons of sugarcane bagasse is produced annually [10]. Traditionally, the produced bagasse is used for onsite heat and electricity generation by most large and medium sized sugar mills [11]. In 2015-16, the major fuels resource used for electricity generation in Australia are coal (63%), uranium (22%) and natural gas (20%) [12]. Renewable energy accounted 12% of the total energy demand in 2012 and is projected to increase to 15% by 2030 [13]. Among the renewables, hydro power accounted for 7% of total generation followed by wind (5%) and solar (3%), almost all of this was small-scale PV [13]. However, the Department of

Environment and Energy has set a target for large-scale generation of 33,000 GWh in 2020 [14]. This means that about 23.5% of Australia's electricity generation in 2020 will be from renewable source.

Decentralised energy generation is considered to solve many problems associated with the increasing in energy demand and costs. In order to adopt new technologies, it must be affordable, easy and safe to operate. Among the biomass-to-bioenergy conversion technologies, various potential thermo-chemical technologies were found to harvest energy from sugarcane bagasse, which include combustion, pyrolysis and gasification [15, 16]. These processes are mainly used to convert biomass into energy-dense bio-fuels namely char, bio-oil and non-condensable gasses [17]. Depending upon the process conditions and feedstocks used, thermo-chemical decomposition may produce different products and ratios.

Pyrolysis is defined as the thermo-chemical decomposition of organic material to produce an array of solid, liquid and gaseous products [18]. Thus, it is an attractive option for managing organic waste since it results in significant waste volume reduction and the production of value added products such as bio-char, bio-oil and synthetic gas. The yield of each product however varies, and is dependent on the pyrolysis method, the feedstock properties, the heating rate, the final temperature, particle size as well as the catalytic agent used [19-21]. Depending upon the process conditions, pyrolysis is classified as fast/flash, slow and vacuum pyrolysis. Fast pyrolysis is optimized for high bio-oil yield, while vacuum pyrolysis is optimised for more even spread of solid bio-char, bio-oil and syngas. On the contrary, slow pyrolysis is optimised to yield bio-char as the main product [22]. The char can be upgraded to a high-value product called activated carbon, and is also used by the sugar industry to clarify raw sugar for white sugar production.

Bio-oil, also known as bio-crude or pyrolysis oil, is an energy product of the pyrolysis process that can be easily stored for short time periods, transported and handled [23]. It can be used in the same way as crude oil and be upgraded to be used as a substitute of heavy fuel oil (bunker oil) [4] or as a substitute to lower the crude oil consumption [24].

It can also be upgraded using catalytic conversion to produce lighter transportation liquid fuels [3, 25, 26]. In fact, fast pyrolysis process can convert up to 75% of the feedstock to a bio-oil intermediate suitable for motor fuel [27]. Other uses of the product include pharmaceutical and cosmetic production. Most of the research on bio-oil production through pyrolysis process was focused on the yield of the bio-oil and/or syngas [28, 29], especially by varying the pyrolysis temperature from 400°C to 650°C [30, 31]. However, the energy density of the bio-oil is affected by several factors such as the parent biomass, the final temperature, heating rate, etc.[4]. Life cycle analyses showed that optimising the yield does not necessarily result in optimum energy returns [32, 33]. Research into efficient energy content of the bio-oil which would lead to a useful fuel for modern transportation road vehicles is therefore needed. The overall efficiency should take into account the overall energy balance of the system using life cycle approach. However, no or limited literature was available on the impact of temperature on the quality of bio-oil. This presents an excellent opportunity for the research team to make a significant impact in this field. This research is thus focused on the investigating the impact of temperature on the oil quality obtained during the pyrolysis of sugarcane bagasse.

To achieve this, the research follows a practical approach and investigates the optimum process condition in terms of temperature and residence time to maximise the bio-oil quality in a simple fast pyrolysis process. A possible reactor design was proposed (Chapter 3.2.1) and the possibility of engaging catalysts to aid the process was discussed (Chapter 4.2.2). Energy and mass balance was carried out.



## **1.1 Aim and Objectives**

The aim of this thesis is to investigate the effect of temperature on the bio-oil quality obtained through fast pyrolysis of sugarcane bagasse. As previous research has focused on maximising the yield, the research question arises if by increasing the quality of the oil, the overall energy gain will be higher than a higher yield output.

The objectives of this research project are:

- To study the effect of heating rate and temperature on bio-oil quality and chemical properties during pyrolysis of sugarcane bagasse at 400 to 600°C.
- To carry out mass and energy balance of the pyrolysis products.

## 2 Literature Review

World energy demand is rising very quickly, due to more electrical and electronic devices in domestic and also industrial environment. By 2030 the world energy demand is forecasted to approximately 700 TJ (Terra Joule) in comparison to approximately 500 TJ today (Figure 1), this is an increase of 40%.

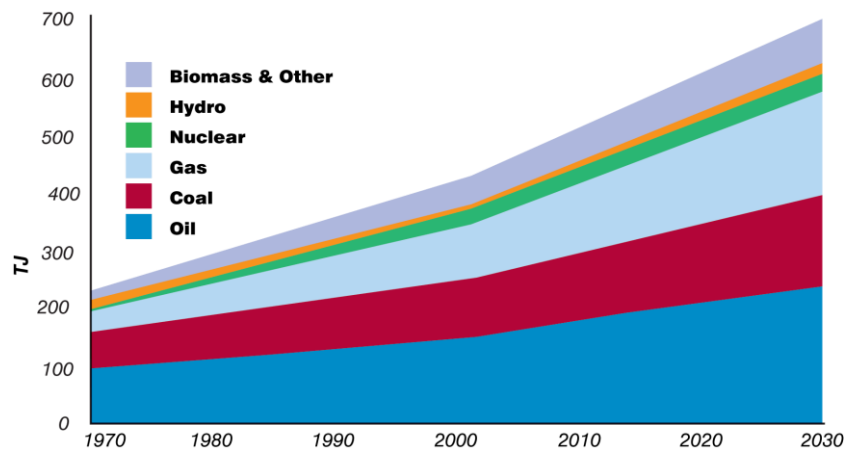


Figure 1: World energy demand forecast [34]

Although there is no exact date for depletion of the world's fossil fuel resources the reserve depletion times for oil, gas, and coal could be already within decades and not centuries [35-37]. In order to satisfy the rising energy demand, renewable energy became more and more popular in the world. For example in Australia, the landfill gas industry produces 850 million kWh from gases captured from waste, enough to supply 120,000 homes with energy. In addition, to improve sustainability and productivity, carbon price returns will help fund AU\$1.7 billion of investment in land sector measures over the next six years [38].

## 2.1.1 Significance of research project in regard to the Australian waste management

Countries worldwide and especially in Australia produce drastically more waste year after year, even when the country population does not increase significantly (Figure 2). There are basically three ways to handle the waste:

- 1) Landfill, which is an environmentally unfriendly solution.
- 2) Recovery / Recycling of waste
- 3) Export to other countries where the waste either gets recycled or goes into landfill

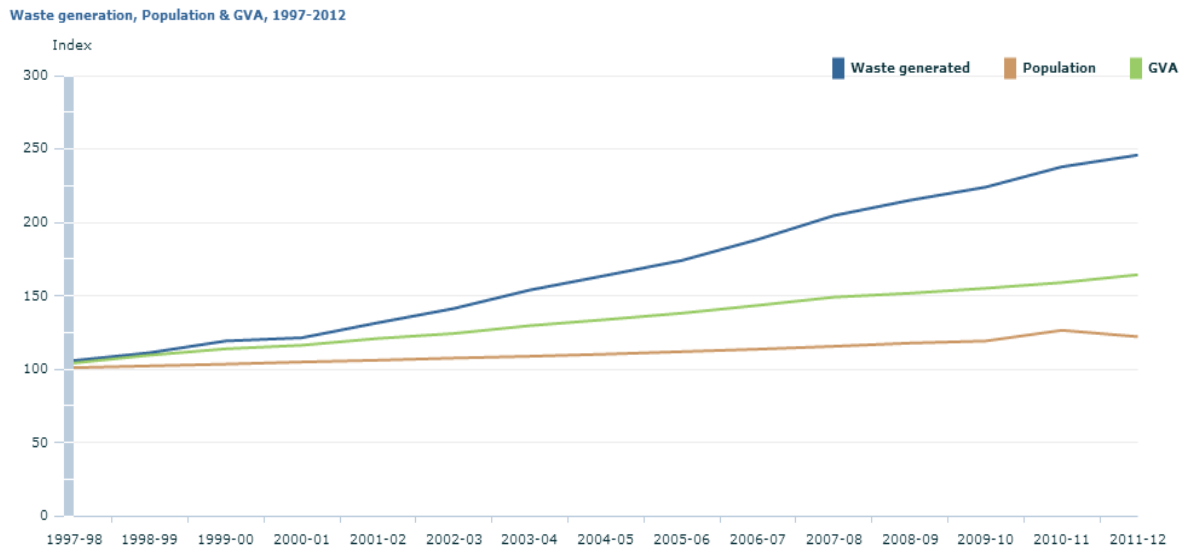
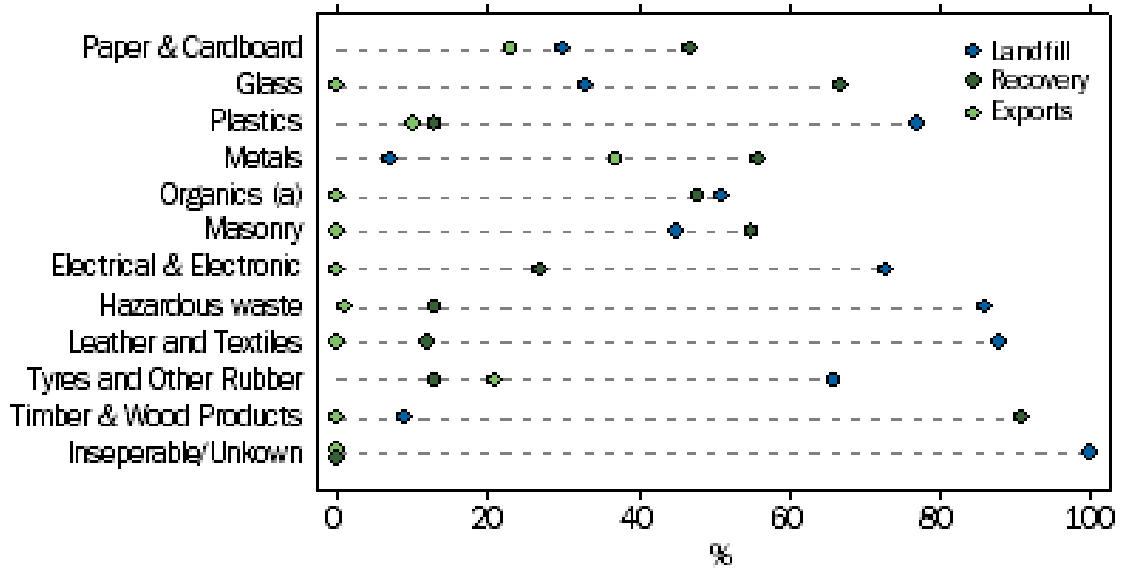


Figure 2: Rate of Australian waste generation compared to Gross Value Added (GVA) and population growth. From 1997 to 2012 [39]

Figure 3 gives an overall indication of different classes of waste and how it is managed in Australia. Pyrolysis can potentially reduce organic waste and some sorts of plastic waste. It can be seen that organic waste shows a very high recovery rate, were as timber and wood products are normally put into landfill. This research project is focused on organic materials as feed stock. However, it can be noticed that around 80% of the Australian plastic waste goes into recovery.



(a) Doesn't include timber

Figure 3: Waste Management by Material (% of material total generation) 2009-10 [39]

Overall, it can be seen that the value of Australia's waste exports has tripled in the last decade (Figure 4). This includes waste, which can be easily used for energy production, instead of spending money on transportation to another country and therewith using up more fossil fuel resources.

International Trade in Waste (tonnes), 1990-2012

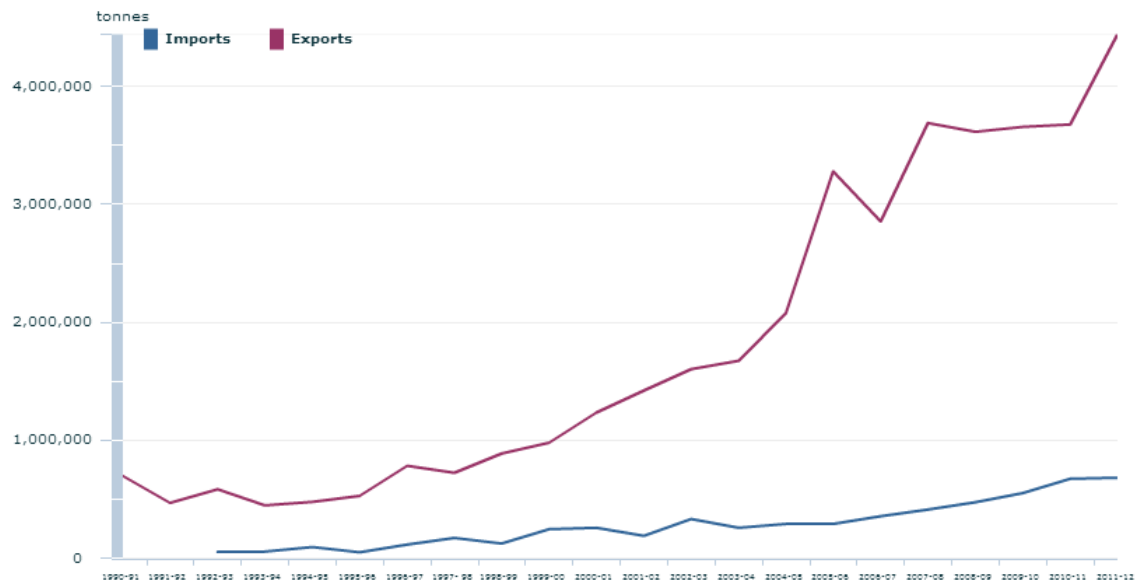


Figure 4: Australian International Trade of Waste [39]

## 2.1.2 Significance of research project in regard to energy production

Certain feed stocks such as are quite dense (up to  $515 \text{ kg/m}^3$ ) and have a heating value of  $20 \text{ MJ/kg}$ . By using those organic feedstocks alone, an electricity output of more than  $250,000 \text{ MWh}$  per annum would be possible [40], depending on the region and feedstock used. This shows that, just by utilizing organic waste, enormous amounts of energy can be retained and together with other renewable energy resources such as solar, wind etc. prevent an energy crisis. The advantage of this renewable energy source is that the energy is available on demand, whereas for other common renewable energy sources such as solar PV solar radiation is needed, which is only available during the day at different intensities and also not during peak times in the evening.

As pointed out in the introduction, the pyrolysis process of sugar cane bagasse to attain gas and bio-oil to generate energy would create an excellent opportunity to reduce the landfill of agricultural waste and produce environmentally sustainable energy at the same time. In order to satisfy the agricultural demand of a growing earth population it can be seen that within seven years the sugar consumption has increased significantly (Figure 5). Most of the gross weight is solid waste by producing sugar, which can be used to create bio-energy products.

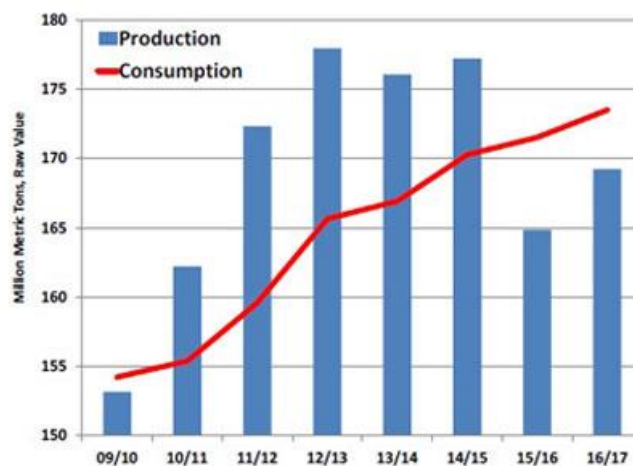


Figure 5: World Sugar consumption [41]

Agriculture has been identified as an important economic growth area for Australia. However, to achieve a sustainable growth, solutions are needed for managing the waste in an economic and environmentally responsible way. Bio char, a product of the pyrolysis process, can be used as a soil amendment and thus reducing fertilizers use. Pyrolysis can also play significant role in the sustainability of the agriculture industry.

This project will contribute to the sustainability of the agriculture industry by:

- Provide a stepping stone towards the development of an environmentally responsible and more streamlined process for managing the organic waste.
- Contribute towards the economic sustainability of regional Australia.
- Producing high energy content bio oil as potential biofuel for vehicles. This will lead to a reduction in fossil fuel consumption.

Different heating methods have been investigated together with the optimum times for increasing the energy yield of the bio fuel. Current research only shows the maximum quantity of the oil. By increasing the energy content however, the bio fuel could fulfil the current car industry requirements for biofuel [42].

The advantages of the power generation via pyrolysis are: Reduces landfill, low carbon emissions in comparison to other energy generation methods, substitute's coal, gas and oil, modular system, more efficient than the incineration power generation method and quicker than the digestion method. However, there are also some disadvantages, such as high capital costs and more maintenance than environmental unfriendly methods, but only because of the oil acidity level which can result into corrosion of the tanks, as well as potential gas pollutants if the syngas is not flared or captured for energy use.

## 2.2 Biomass Theory and Pyrolysis Output

Depending on the feedstock, the output of the pyrolysis process differs strongly. Previous papers were intensely focused on the yield of the oil, char, and gas, of different feedstocks, by varying maximum heat, heating ramp, and therewith residual times as well as moisture content [27, 43, 44] and the oil quality was improved with pre-treatment [45] or via upgrading [46-48]. Overall, the yield of bio oil, char, and gas can be calculated as follows [49]:

$$\text{Yield\%} = \left[ \frac{\text{Desired product (bio-oil or char, g)}}{20 \times (1 - (\% \text{ash} + \% \text{moisture}))} \right] \times 100 \quad (1)$$

The next sub-chapters deal with the feedstock by using sugarcane bagasse and the overall composition of Biomass.

### 2.2.1 Sugarcane Bagasse

Sugarcane bagasse originated from a C4 plant which has been crushed and then through the addition of water subtracted of the sugar inside the plant. In chapter 0 Figure 5 it can be seen how the sugar cane industry has steadily increased production over the years and countries such as Brazil produce over 160 million tonnes per year [50]. Because of the high lignin content of sugarcane bagasse showed in chapter 2.2.2, the composting process through cellulolytic microorganisms would take a very long time [51]. A more common method is to burn the bagasse in order to heat and/or drive a turbine for producing energy and use the ash either as fertilizer or even as a sand substitute in concrete [52] or other products which would normally require sand [53]. Although, the GHG emissions for producing electrical energy are much lower in comparison to conventional fossil fuels [54], from one tonne of sugar cane bagasse, only 0.3 tonnes can be used for the combustion process [55]. By putting sugarcane bagasse through the pyrolysis process, one can use 100% of the feedstock and obtain gas, which can potentially be used to reheat the system, char, which can be used as fertilizer, sand substitute etc. and bio-oil. Bio oil has the advantage that it is highly versatile and

portable, thus it can be used to heat, in a generator to produce electrical energy or directly in the transportation sector for diesel engines. As sugarcane bagasse is available as a waste product in enormous quantities nowadays, this feedstock is chosen for this project and compared to other feedstocks in the next chapter.

## 2.2.2 Composition of Biomass

Alongside other contents such as water, there are basically three major components of biomass [56, 57]:

- Cellulose  $(C_6H_{10}O_5)_n$  , where  $n=500-4000$
- Hemicellulose  $(C_5H_8O_4)_n$  , where  $n=50-200$
- Lignin, consisting of highly branched, substituted, mononuclear aromatic polymers, often bound to adjacent cellulose and hemicellulose fibres to form a lignocellulosic complex.

All three components have different thermal decomposition behaviours, which can be determined by the thermal gravimetric analysis (TGA) and are present in different concentrations in different feedstock. Sugar cane bagasse has a composition of 23 - 32% Lignin, 19-24% Cellulose, and 32-48% Hemicellulose, as it can be seen in Table 1. Previous research investigated that at approximately 500°C, which would be in the temperature range of the fast pyrolysis process, the most bio oil was harvested from the cellulose content of the feedstock [58].



Table 1: Feedstock composition [59]

<b>Feedstock</b>	<b>Lignin (%)</b>	<b>Cellulose (%)</b>	<b>Hemicellulose (%)</b>
Wood	25–30	35–50	20–30
Wheat straw	15–20	33–40	20–25
Switch grass	5–20	30–50	10–40
Sugarcane bagasse	23–32	19–24	32–48
Miscanthus	17	24	44
Corn stover	16–21	28	35
Hazelnut shell	42.9	28.8	30.4
Olive husk	48.4	24	23.6
Corn cob	15	50.5	31
Tea waste	40	30.20	19.9
Walnut shell	52.3	25.6	22.7
Almond shell	20.4	50.7	28.9
Sunflower shell	17	48.4	34.6
Nut Shell	30–40	25–30	25–30
Paper	0–15	85–99	0
Rice straw	18	32.1	24
Stored refuse	20	60	20
Leaves	0	15–20	80–85
Cotton seed hairs	0	80–95	5–20

The relatively high component of aromatics, such as ethylbenzene, styrene etc., in the oil of sugarcane bagasse and oil from other pyrolysis feedstocks such as olive husk, walnut shell etc. can cause two negative impacts on the oil. The first negative impact is the formation of solids over longer storage duration and the second negative impact is the usage of the fuel in an engine [60], which can cause failure of engines by using fuel with high aromatic content due to solid deposits, but also causes an increase in NO<sub>x</sub> emissions.[61, 62]

Furthermore, by analysing the feedstock components, the Higher Heating value (HHV) or gross heating value can be determined, which includes the heating value of all impurities as well (Table 2).

Table 2: Feedstock comparison for fast pyrolysis process (Elemental analysis is on a dry weight basis (db)) [4, 63, 64]

	Oak	Switchgrass	Alfalfa Stems	Corn Stover	Barley Straw	Barley Hulls	Chicken Litter	Sugarcane bagasse
Total Water Wt %	22.3	15.8	28.6	9.2	26.7	13.8	20.1	25.4
PH	2.6	3.1	2.3	2.9	2.4	2.5	6.9	2.6
Elemental Analysis (db)								
C (wt%)	58.13	47.47	56.84	53.97	50.78	54.37	55.64	48.64
H (wt%)	6.07	6.96	7.86	6.92	3.20	5.32	7.19	5.87
N (wt%)	1.50	.036	3.73	1.18	1.37	1.79	7.77	0.16
S (wt%)	0	-	0.07	<0.05	0.00	0.09	0.70	0.04
O (wt%)	34.30	45.19	31.30	37.94	44.42	38.49	29.27	42.82
HHV (MJ/kg)	18.1	18.4	20.6	24.3	17.7	20.8	23.3	18.99
HHV (MJ/kg, db)	23.3	21.9	28.9	26.7	24.2	24.1	29.2	24.1

### 2.3 Biomass to bioenergy technologies

To retain energy from biomass, there are four major methods [65] with subsequent methods:

1. Thermal conversion, with or without the presence of oxygen, including:
  - Direct combustion
  - Pyrolysis
  - Torrefaction
  
2. Thermochemical conversion is the combination of heat and chemical processes
  - Gasification

3. Biochemical conversion involves use of enzymes, bacteria or other microorganisms to break down biomass into liquid fuels
  - Anaerobic digestion
  - Fermentation
  
4. Chemical conversion encompasses the use of chemical agents to convert biomass into liquid fuels, so that Triglyceride with an alcohol bonding through a catalyst results in methyl ester and Glycerol.
  - Transesterification
  - Esterification

Focus of this research project is the energy content of the oil output. In Table 3, different optimum methods are listed in order to capture methanol and bio-methanol. It shows that for liquid methanol and bio-methanol, pyrolysis is an ideal solution.

Table 3: Main production methods of methanol and bio-methanol [66]

<b>Methanol</b>	<b>Bio-Methanol</b>
Catalytic synthesis from CO and H <sub>2</sub>	Catalytic synthesis from CO and H <sub>2</sub>
Petroleum gas	Gaseous products from biomass gasification
Natural gas	Synthetic gas from biomass and coal
Distillation of liquid from coal pyrolysis	Distillation of liquid from pyrolysis

### 2.3.1 Biochemical Process

The Biochemical conversion of organic waste is realised by breaking down molecules with the help of bacteria enzymes and other microorganisms. One of the oldest and most

popular ones is composting [67], not only used for industrial purposes but also used in many private households and gardens . A metabolic process named fermentation, where sugar is converted to acids, gases or alcohol through microorganisms [68], and anaerobic digestion which also makes use of microorganisms but with the absence of oxygen [69, 70]. Composting is the easiest but also the slowest process, by having the feedstock stored on a pile and perhaps watered to increase the process speed, whereas the focus here is on the earth fertilizer end-product. The different steps of the fermentation process can be visualized in Figure 6. and also used for the anaerobic digestion if the oxygen is replaced by an inert gas.

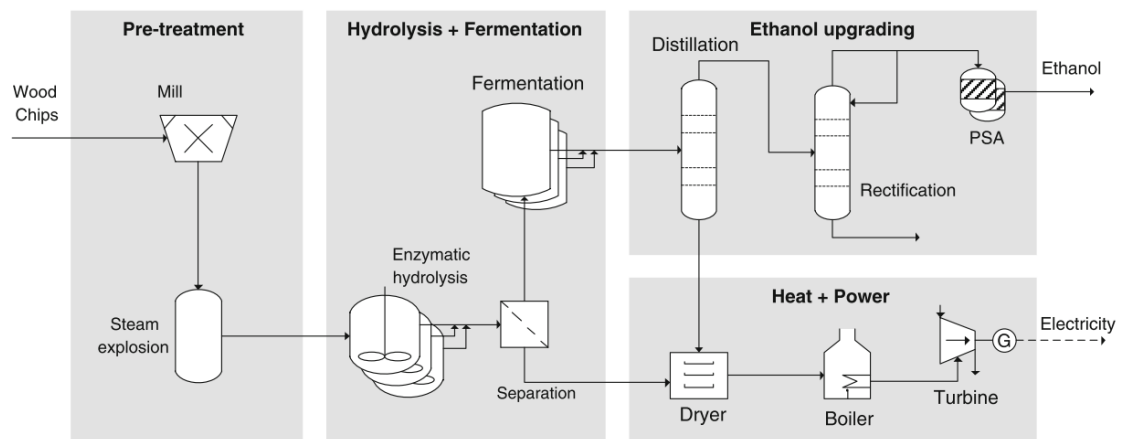


Figure 6: Process flow sheet for biochemical conversion with hydrolysis and fermentation [71]

### 2.3.2 Thermochemical Process

Thermochemical processes are for example Combustion, Pyrolysis, and Gasification [56, 71] (Figure 7). Combustion is one of the oldest forms of obtaining energy from fossil fuels and other feedstock.

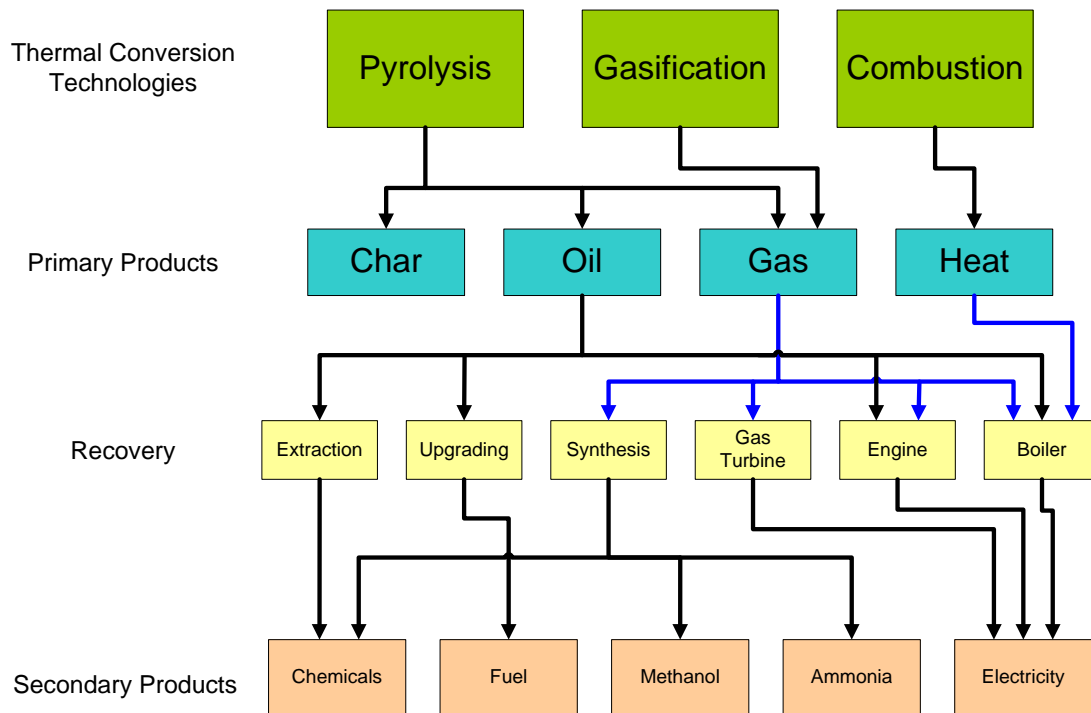


Figure 7: Thermal Conversion Technologies

Gasification uses organic or inorganic feedstock with the presence of air/oxygen to produce gas [72] (Figure 8) and is sometimes also combined with biochemical processes such as fermentation (Figure 9). Pyrolysis has a very versatile feedstock organic and inorganic. As organic feedstock woodchips, which are the most popular feedstock [73], other organic waste such as olive waste [4, 74], and corn [75-77] are very popular. For inorganic feedstock, PCBs [78] and rubber materials [79, 80] are often used. The pyrolysis process has a very broad output of primary products such as char, oil, and gas, which is broader than the other thermal conversion processes, and so is its utilization (Figure 10).

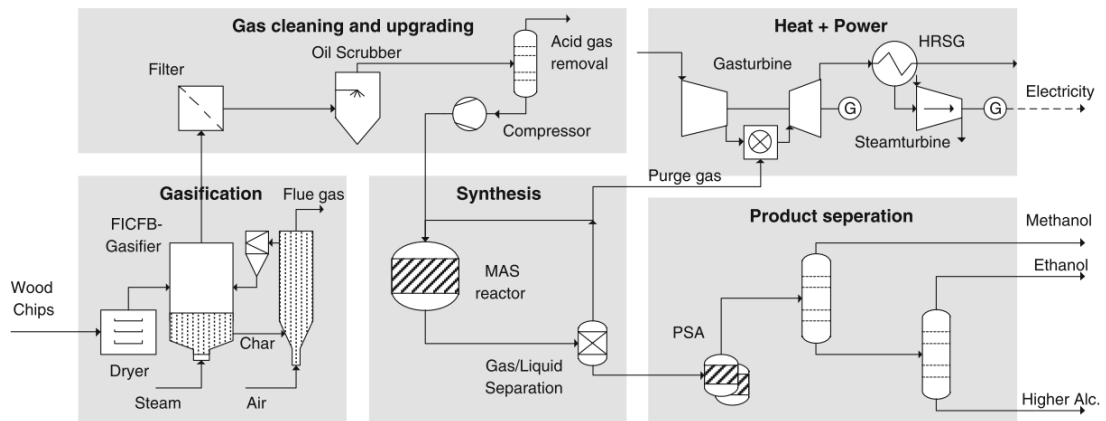


Figure 8: Process flowsheet for thermochemical conversion with gasification and synthesis [71]

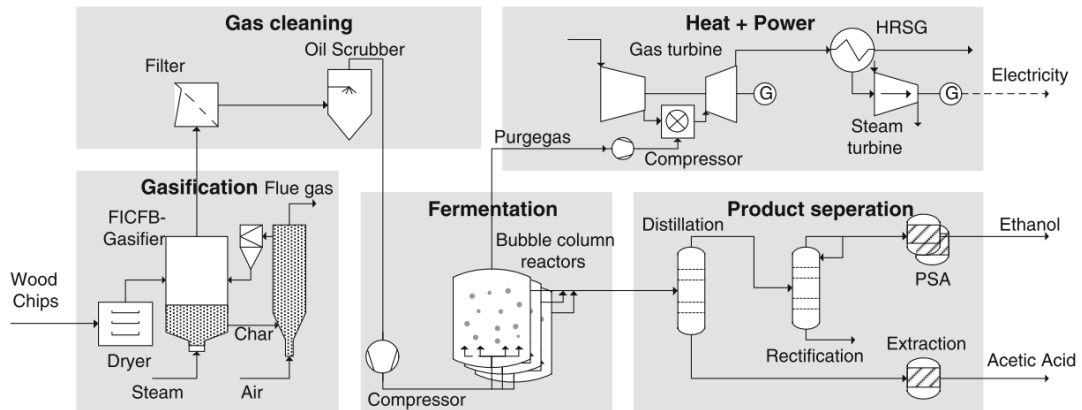


Figure 9: Process flowsheet for thermochemical conversion with gasification and syngas fermentation [71]

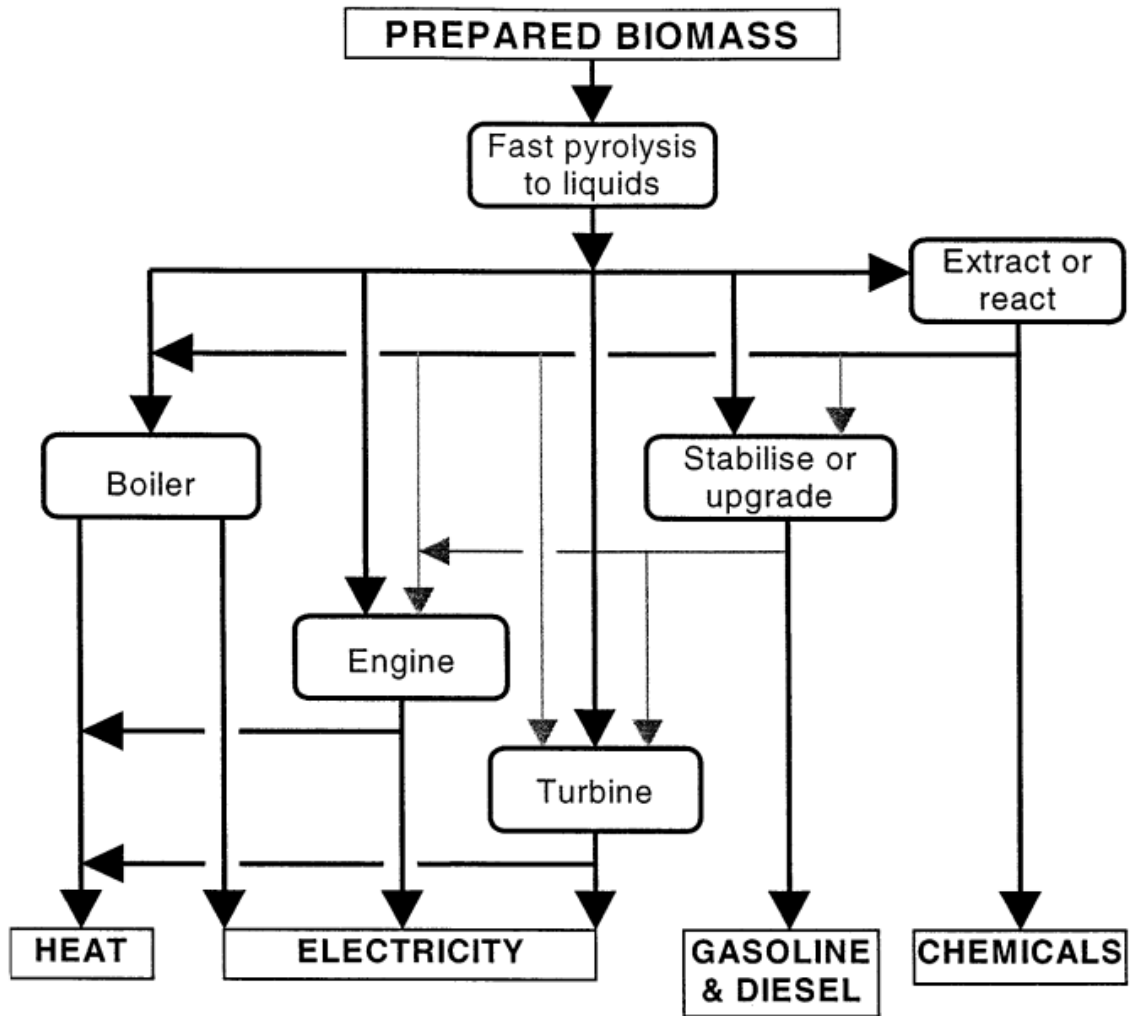


Figure 10: Usage of Pyrolysis Bio-Oils [81]

## 2.4 The Pyrolysis Process

The common definition of Pyrolysis is described as:

“Pyrolysis is thermal decomposition occurring in the absence of oxygen. Lower process temperatures and longer vapour residence times favour the production of charcoal; high temperatures and longer residence times increase biomass conversion to gas; and moderate temperatures and short vapour residence time are optimum for producing liquids which are widely referred to a bio-oil [82]. The whole process can be visualised as follows:

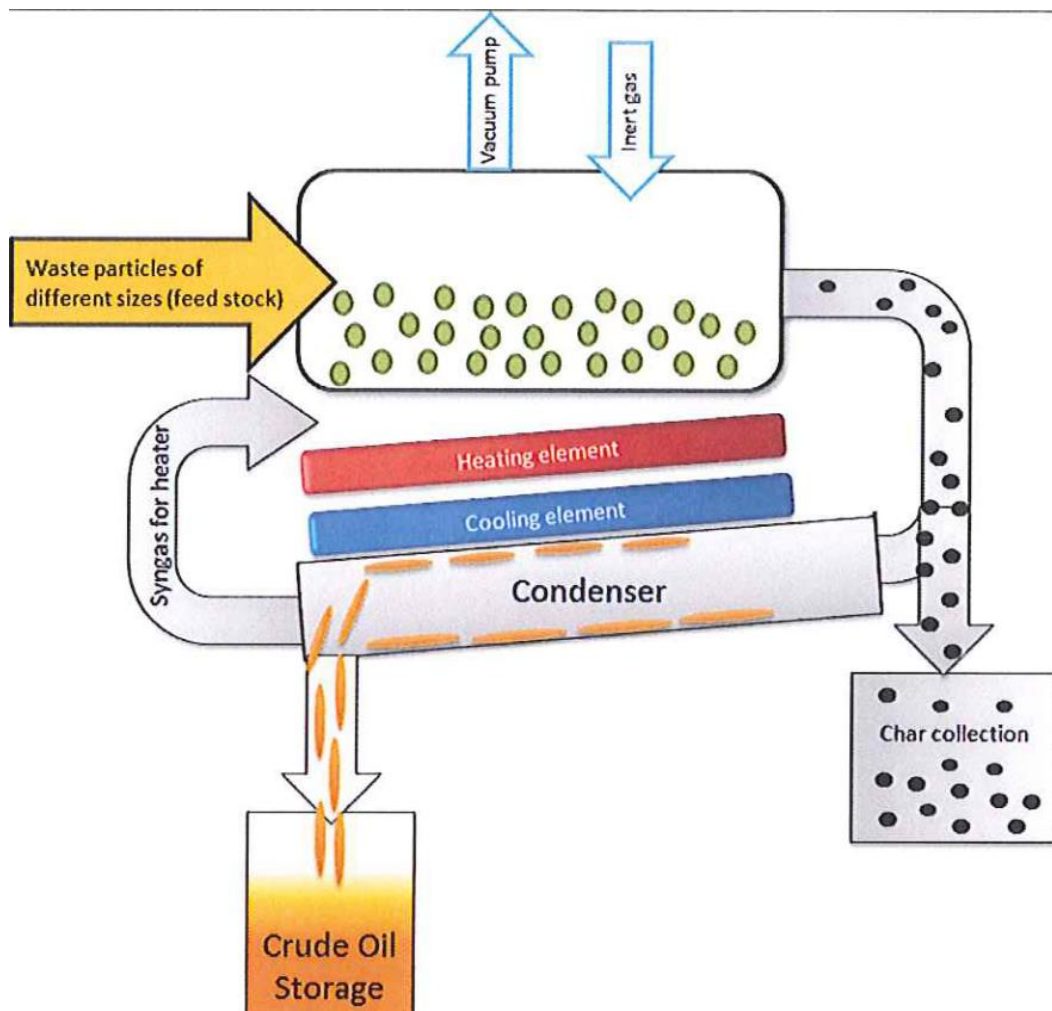


Figure 11: Common pyrolysis process



Feedstock is placed into the reactor and under absence of oxygen the feedstock is heated up. The produced vapour then goes through an (optional) cyclone to collect the impurities and additional char, while the vapour passes through and flows to the condenser, where the oil is condensed and captured. The gas is then either captured or used for self-maintaining the process. By employing the pyrolysis method we can derive three different outputs: Bio-oil, Bio-char, and Syngas (Figure 12). The most important factors are residence time as a result of the temperature, heating rate, and particle size (Table 4).

Table 4: Pyrolysis type comparison [72, 83, 84]

Pyrolysis Process	Solid Residence Time (s)	Heating Rate (K/s)	Particle Size (mm)	Temp.(K)	Product Yield (%)		
					Oil	Char	Gas
Slow (conventional )	450-6000	0.1-1	5-50	550-950	30	35	35
Fast	0.5-10	10-200	<1.5	850-1250	50	20	30
Flash	<0.5	>1000	<0.2	1050-1300	75	12	13

Depending on those factors, pyrolysis methods can broadly be classified into slow, fast and flash methods. Slow pyrolysis is traditionally used to produce charcoal [18] while the faster pyrolysis methods are employed to maximise bio-oil production [85].

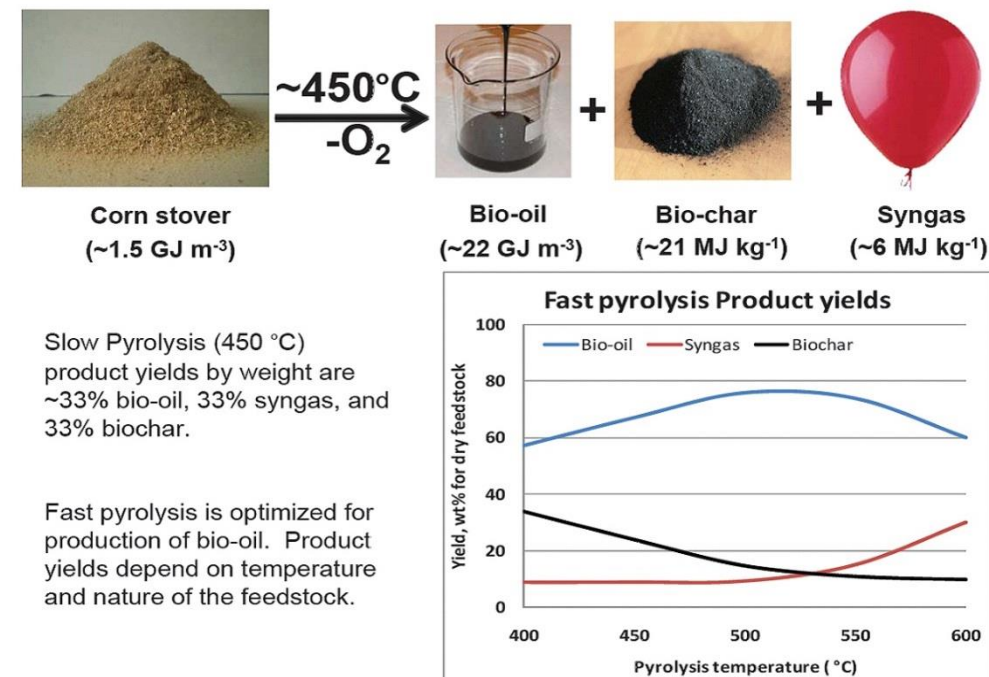


Figure 12: Output example of Pyrolysis method [86]

After determining the 1 parameters, pyrolysis further experiments will be conducted on larger samples using the same pyrolysis test rig (Figure 13). These experiments are then used to study the scalability of the results obtained from the small scale experiments and potentially tweak the parameters to achieve optimal process for the design of pilot scale reactor. They are also used to generate larger quantities of biochar in order to extent the project to further experiments in this area (seed germination and plant growth).

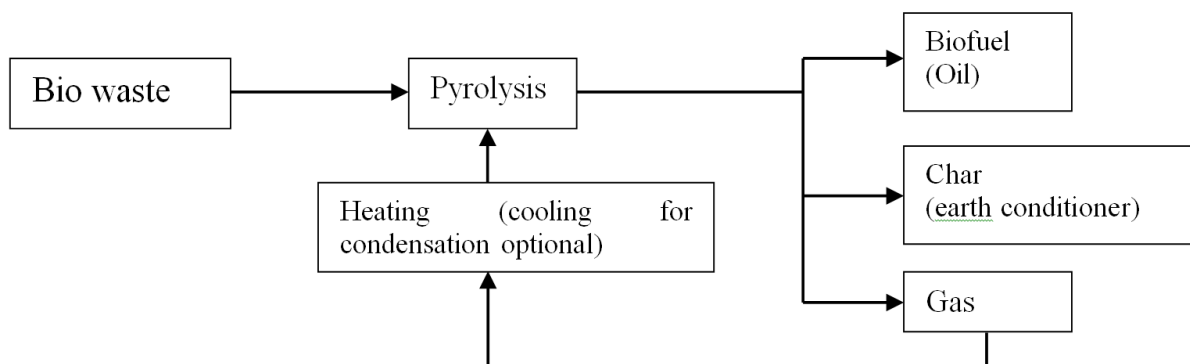


Figure 13: Pyrolysis test rig

Pyrolysis experiments in this research project are carried out on small samples of bio waste, to determine the impact of varying pyrolysis parameters such as final temperature, heating rate, residence time...etc. on the quality of the final product.

#### **2.4.1 Factors affecting the pyrolysis output**

There are various main factors which can affect the overall pyrolysis output, which include the type of feedstock, also shown in Table 1, which through different composition of Cellulose, Hemicellulose, Lignin can affect the oil output significantly [87-89]. The size of feedstock [90] as well as moisture and other foreign material content [91] can also affect the oil output and causes even the forming of damaging residues into the oil.

In addition to the feedstock properties there are various factors in how the pyrolysis process is conducted and this includes, type and material of the reactor [92] as well as the use of catalysts [93]. The use of potential catalysts will be discussed later in chapter 4.2.2, but due to saving costs and fulfil the aims of the research mentioned earlier in chapter 1.1, the actual use of catalysts for this project is not investigated. However, when the amount of feedstock increases, the use of such a catalyst might be beneficial, to provide an even and fast heat distribution to the feedstock. Furthermore, for the same cost saving reasons and thus make the process mainstream capable and realistic, the moisture content of the feedstock is at normal storage environment as well as the particle size should be left as is. The specific factors effecting oil output will be discussed in the next paragraph. Furthermore, the operation itself such as the maximum temperature and heating ramp [92], are one of the obvious factors which can be controlled in order to influence the quality of the output.

### 2.4.1.1 Oil Output

A typical bio oil composition is shown in Table 5, which shows that the water content is with up to 30% and a very high content of combined aromatics is too impure for direct operation in an engine/generator. However, with the design of the reactor, those impurities can be reduced.

Attention must be paid to the duration of the heating ramp and maximum temperature of the vapours through the transfer lines from the pyrolysis reactor to the storage container as well as the separation of char from the oil vapours before condensation [94].

The effectiveness of the transfer lines and condensation equipment is a very important factor to filter out undesirable components from the gas stream, which are low molecular weight esters, ethers, acetals, alcohols, aldehydes and water. Those contaminations of the bio-oil can potentially cause corrosion of storage containers. Furthermore, if the transfer lines and sections are too long, the vapour might condensate and resides at locations inside the system, was they form aromatics, which over a long period of time form to wax which is a potential hazard for machines.

Table 5: Typical bio-oil composition of bio crude oil [95]

Major Group	Compounds	Mass (%)
Water		20–30
Lignin fragments	Insoluble pyrolytic lignin	15–30
Aldehydes	Formaldehyde, acetaldehyde, hydroxyacetaldehyde, glyoxal, methylglyoxal	10–20
Carboxylic acids	Formic, acetic, propionic, butyric, pentanoic, hexanoic, glycolic	10–15
Carbohydrates	Cellobiosan, $\alpha$ -D-levoglucosan, oligosaccharides, 1.6 anhydroglucofuranose	5–10
Phenols	Phenol, cresols, guaiacols, syringols	2–5
Furfurals		1–4
Alcohols	Methanol, ethanol	2–5
Ketones	Acetol (1-hydroxy-2-propanone), cyclopentanone	1–5

**Source:** Adapted from Bridgwater et al. (2001), p. 989.

Appendix 4 and 5 provide a more detailed composition of bio oils.

Besides the feedstock and the reactor type it is evident that the temperature is the main factor in regard to the oil-output. Previous research showed that the highest bio oil yield was achieved at around 550°C [96]. By conducting vacuum pyrolysis with sugarcane bagasse at very low temperatures below 100°C it was shown that the oil quality was very poor [97], thus very low temperatures will not be considered for this Master project. The temperature as well as the heating ramp determines the different types of pyrolysis. These types are discussed in the next chapters.

### **2.4.2 Traditional (Slow) Pyrolysis**

Slow Pyrolysis is the first of the discussed methods which has been used for a very long time to harvest energy from Bio mass and split it into bio-oil, char, and gas. The relatively long heating rate, combined with, in comparison to fast and flash method, low process temperature and large particles causes a high solid residence time and thus a long vapour phase. This results into polymerisation of reactive components, where the oils boiling point already starts below 100°C, whereas the distillation stops at 250°C [98]. Although, this does not affect the oil yield, this will result into bigger amount of solid char and other not wanted liquid substances and thus lower the oil quality [99]. In addition to that, the longer heating times and will result into more energy losses or higher financial burden because of better reactor insulation to avoid heat loss over time [100].

### 2.4.3 Fast and Flash Pyrolysis

Fast pyrolysis methods are widely used when the focus is on maximising the liquid yield of the process and mostly used with three types of reactors: Fluidized bed reactors, mechanically mixed, and ablative reactors [101].

The main parameters of a fast pyrolysis process are [102]:

- Finely ground biomass feedstock requirements for high heating rates and rapid heat transfer rates
- Cautiously controlled temperature range
- Vapours need to be rapidly cooled down for good quality bio-oil output

The optimum temperature for the highest oil yield can be determined at around 450°C which results, depending on the feedstock, in 69.2 wt% oil output with a water content of 34.5 wt%, whereas at a temperature of 550°C a vast increase of aromatic hydrocarbons (toluene, xylenes and trimethylbenzenes) can be recognised [103]. However, this is also depending on the feedstock. While HZSM-5 (which are also producing the highest hydrocarbon yield at approx. 28%) and H-mordenite are responsible for producing aromatic hydrocarbons, H-Y, silicalite and silica-alumina produce more aliphatic hydrocarbons [104, 105].

### 2.4.4 Reactor Types

The reactor is the most important part in the pyrolysis process [59]. Over the reactor almost every important variable of the pyrolysis process can be controlled including the heating rate, maximum temperature vapour residence times etc.. The type of reactor also defines the suitability for different feed stocks but most importantly the output yield and quality of gas, oil and char results. The research project focus is on the bio-oil quality and thus the pyrolysis performance in this area has the highest priority.

For fast pyrolysis there are various types of reactors [106]:

- Fixed bed reactor
- Bubbling fluidized bed
- Circulating fluidized beds/transport reactor
- Rotating cone pyrolyzer
- Ablative pyrolyzer
- Vacuum pyrolyzer
- Auger reactor

#### **2.4.4.1 Fixed bed reactor**

The oldest type of reactor is the fixed bed reactor. This reactor type is simple, reliable and proven for fuels with a relative uniform size [107]. The set-up normally consists of a container which is traditionally heated by a fire source. However, different heating methods will be discussed in chapter 2.4.5. Due to the fact that the feedstock stays fixed inside the reactor, homogenous heat transfer within the feedstock is difficult and thus this reactor is suitable for small scale applications. The container has normally one feedstock input and one or two outputs for ash removal as well as gas output.

#### **2.4.4.2 Fluidized bed**

There are two versions of fluidized bed reactors the circulating fluidized bed reactors and the bubbling fluidized bed reactors. They both provide good temperature control as well as heat transfer due to a floating sand bed. The yield and quality of bio oil with approximately 70 to 75% dry basis biomass is excellent and the best of all pyrolysis reactors [108, 109]. However, therefore it needs particle sizes of less than 3mm [109]. Figure 14 shows a typical model of a fluidized bed reactor.

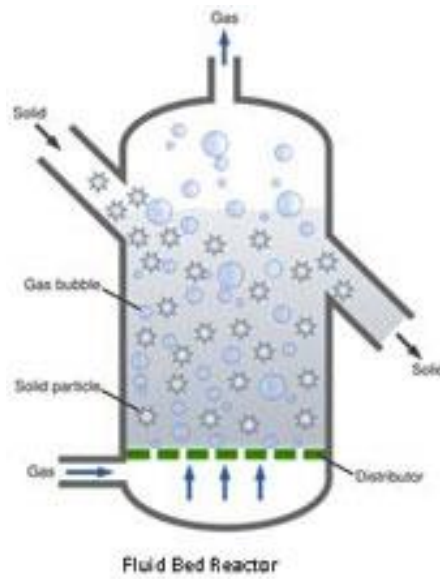


Figure 14: Fluidized-Bed Reactor [110]

### 2.4.4.3 Rotating cone pyrolyzer

The rotating cone pyrolyzer does not need carrier gas and is suitable for small feedstock. Due to the rotating cone, where sand and feedstock is mixed together, the scalability is very restricted but the heat is evenly distributed to the feedstock.

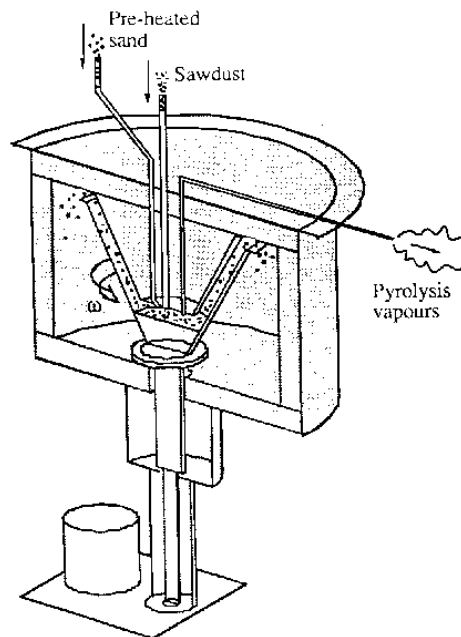


Figure 15: Cross Section of the Rotating Cone Reactor [111]



#### **2.4.4.4 Ablative pyrolysis reactor**

The ablative pyrolysis reactor is similar to the rotating cone reactor. The difference is that the feedstock is pressed against a hot spinning disk instead of the distribution of the feedstock to a cone. This process does not require a carrier gas and due to the 'build in' grinding process, the pre-processing of the feed stock can be waved. For this reactor type and the rotating cone reactor type, motors or engines are used to drive the cone or disk. Thus, these two methods consume electrical energy or fuel which needs to be considered especially if the reactor is used for industrial purposes and has a large size.

#### **2.4.4.5 Vacuum pyrolysis**

Due to the vacuum and therewith the lack of oxygen, the vacuum pyrolysis process does not require any carrier gas. However, temperatures are between 200°C and 400°C and thus not suitable for fast pyrolysis. The lack of sand, gas, or other materials and/or chemicals would result in cleaner oil output. However, these long processing times of slow pyrolysis can cause polymerization of the oil and thus, this process is not suitable for this research project. In addition to that energy will be required in order to operate the vacuum pump.

#### **2.4.4.6 Auger reactor**

For this process an auger inside the heating area is employed to mix sand from one container with the feedstock from another container. Due to that rotating system a large installation would be cost intensive and would also require vast amounts of energy upfront for the system also due to difficulties to transport the heat to the feedstock during the rotating process.

## 2.4.5 Different heating methods for Pyrolysis

Based on the literature review, various heating methods are applied for pyrolysis at the moment, such as:

- Resistive heating
- Inductive heating
- Microwave heating
- Solar heating
- Plasma heating
- Fire heating

All five heating methods have their specific advantages. Resistive heating can be seen as a classical light bulb if it comes to heating, where 5% is emitted as light output and 95% will be converted to heat, where the electrical power  $P_{el}$  is approximately equal the thermal power  $P_h$  and therewith:

$$P_h \approx P_{el} \cdot 0.95 = V \cdot I \cdot 0.95 = I^2 R \cdot 0.95 \quad (2)$$

Thus, the heating efficacy is at around 95%. However, the feedstock close to the heating elements will heat up more quickly than the feedstock in the middle of the container.

Inductive [112, 113] and particularly the microwave heating methods [83, 114, 115] are more efficient for larger feedstock's, as they will penetrate larger mass throughout and hence heat up the feedstock evenly. Therefore this heating method will then result in energy savings.

In addition to the heating methods mentioned above, high temperature Peltier elements were investigated as a potential heat source (Figure 16).

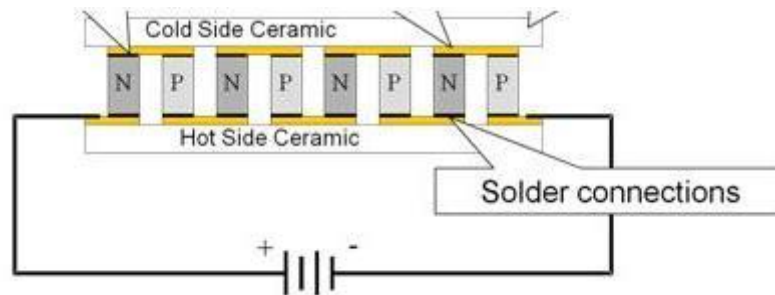


Figure 16: Peltier element [38]

They consist of a solid state PN junction which reacts by connecting a power source to it. The one side of the plate is then heating up and could be used to start the pyrolysis effect itself. The other side of the Peltier element would cool down and could be used for the condensation. In addition to that, Peltier elements are available in different sizes, can be scaled, are available for different voltages, and could be used as a thermal generator after the process has been settled in and the system is self-sustaining. Nevertheless, Peltier elements have an efficiency of around 60% and although there are some “low-cost” high temperature Peltier element experiments [116], those elements are expensive in comparison to traditional heating methods.

Plasma heating develops a very high energy density and thus is suitable for fast pyrolysis due to the high achievable maximum temperature and quick heat transfer. However, this method involves high installation and maintenance costs. Additionally, the amount of electrical energy required to create plasma, including the operation of a vacuum pump, is much higher in comparison to the other heating methods [117].

Solar heating is a free renewable energy source and the energy balance of the whole pyrolysis system benefits of engaging direct solar radiation as such [118]. The feedstock in those systems sits in a reactor surrounded by mirrors and is heated by concentrated solar radiation, shown in Figure 17 [119]. Nevertheless, the whole system is dependent on the weather and might even not be suitable for large areas on the planet due to that. The high installation costs as well as maintenance costs involved for keeping the reflectors clean are disadvantages of such systems. Although, the potential high maximum

temperatures and, under excellent circumstances, rapid heating rates, which would be suitable for the fast pyrolysis process, this method is not suitable for a universal pyrolysis system and therewith not employed in this research project.

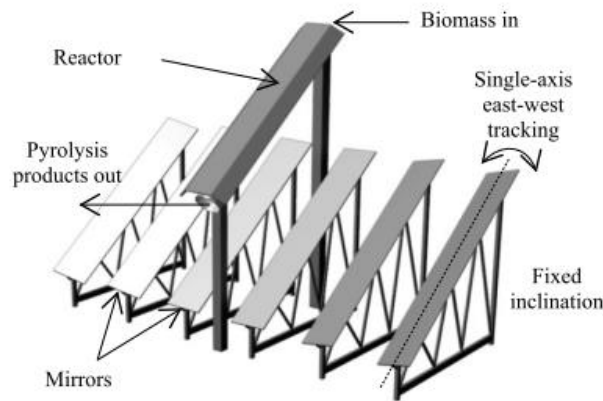


Figure 17: Linear solar pyrolysis reactor setup [119]

Fire heating can be used as a classic method for heating up the feedstock. The advantages here are that the syngas produced by the process itself can aid the heating process, thus it will result into an almost self-maintaining process and consequently reduce the costs. Additionally, produced methane can be burned directly and does not either damage the environment nor needs to be stored in a container. Furthermore, fire heating was found to not only be simple but also very quick in the heating ramp and provides even heating of the feedstock.

The verdict of the above comparison of heating methods is in favour of two methods, the classic fire heating method and electrical heating for the following reasons:

- The focus of this research is on maximising the energy value of the oil, thus quick heat ramps are important to avoid the forming of aromatics
- The feedstock in this research project is relatively small and thus the other methods will not provide any advantages for this project
- Fire heating as well as electrical heating will provide a easily controllable high heating rate as required for fast and even flash pyrolysis (Table 4 on page 20)
- Other methods and especially the microwave method carries some health and safety risks, due to the radiation

- The costs of both heating methods are the lowest in comparison to the other methods, especially when the amount of feedstock increases

## **2.4.6 Other Pyrolysis output considerations**

This research project is focused on the oil quality and optimizing the pyrolysis parameters in accordance to that. However, besides oil output, the Pyrolysis process creates two more, gas ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_6\text{H}_6$ , etc.) and char. In some cases the gas can be used to heat the reactor and thus keep the whole system self-containing. However, this is only suitable for large feed stocks, where enough gas is produced to keep the system running.

The gas can be used to burn it and heat up the reactor, thus the process becomes almost self-containing depending on the reactor type, installation as well as the feedstock amount, continuous supply, and type of feedstock. However, health and safety precautions need to take place, as for example  $\text{C}_2\text{H}_6$ , when mixed with air at 3.0%–12.5% by volume is highly explosive and also the other gases can even cause cancer. The char can be used as fertilizer in the agar industry.

### **2.4.6.1 Storage Stability Problem of Pyrolysis Bio-Fuel**

Bio oil retained from a pyrolysis process can have some stability issues. This is mainly because of those single-phase pyrolysis liquids becoming more viscous are caused by very short reactor residence as well as rapid heating of the feed stock especially in fast and flash pyrolysis processes. The stability of the fuel is dependent on several factors such as temperature and storage time (Figure 18), but also exposure to oxygen, reactions of organic acids inside the oil, which results in Esterification, where the reaction form

esters and water, or transesterification, which is an exchange of alcohol and acid groups inside the oil [94].

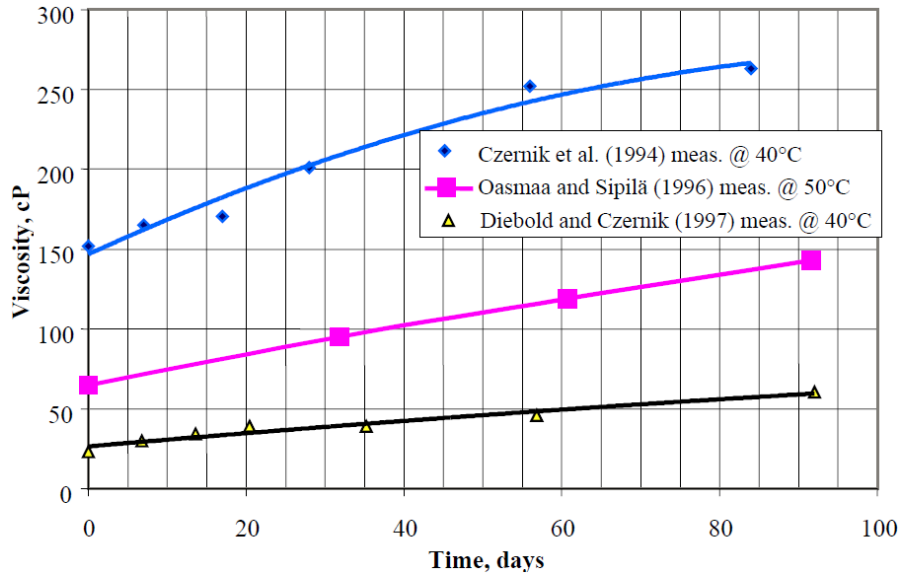


Figure 18: Aging of Bio-Oils at different temperatures [94]

Furthermore, there are several other reactions, such as [94]:

- Reactions of Aldehydes
  - ✓ Homopolymerization
  - ✓ Hydration
  - ✓ Hemiacetal Formation
  - ✓ Acetalization
  - ✓ Transacetalization
- Phenol/Aldehyde Reactions and Resin
- Polymerization of Furan Derivatives
- Dimerization of Organic Nitrogen Compounds
- Sulfur-Containing Compounds
- Unsaturated Organic Reactions
- Alcohol Addition
- Olefinic Condensation
- Oxidation
- Gas-Forming Reactions
- Carbon Dioxide reactions

## 2.4.7 Upgrading of Pyrolysis Bio-Oil Output

This research is focused on the direct output of the raw bio oil and its quality, in order to use is directly in suitable stationary diesel engines (Figure 19). However, in order to increase storage times as well as the stability of the bio fuel and to for the further use in combustion engines, bio oil from a pyrolysis process not only needs certain additives it also requires further process steps such as bio-oil gasification to remove further impurities (Figure 20), fermentation also to reduce the water content (Figure 21), and Hydrocracking to make use of the water content in form of hydrogen production (Figure 22). These processes can slow down the aging of pyrolysis liquids caused by the reactions described in section 2.4.6.1 (Storage Stability Problem of Pyrolysis Bio-Fuel).

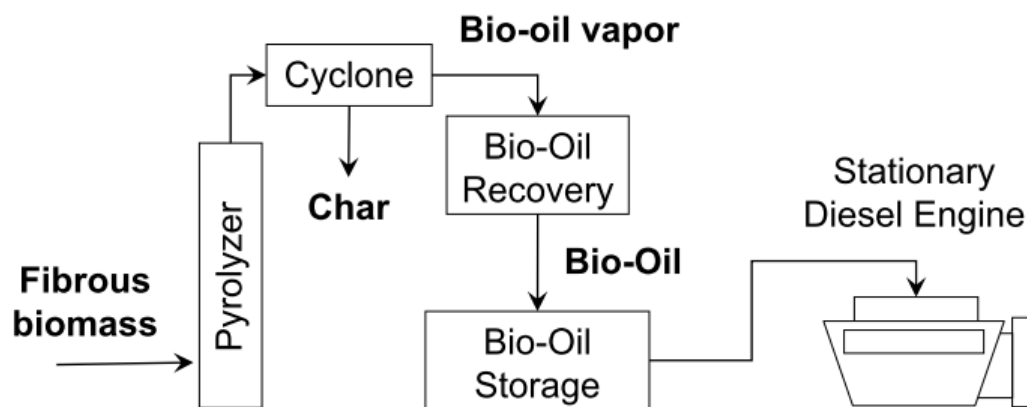


Figure 19: Bio-Oil Usage directly in Diesel Engines [106]

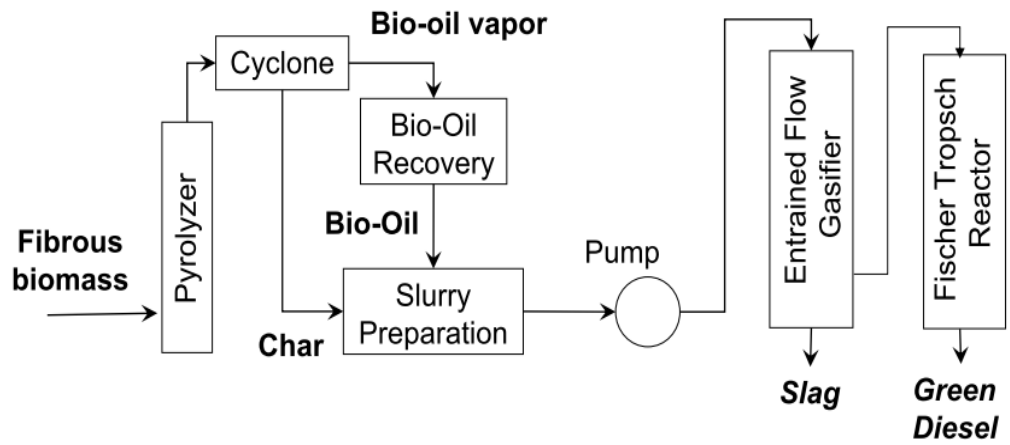


Figure 20: Bio-Oil Gasification [106]

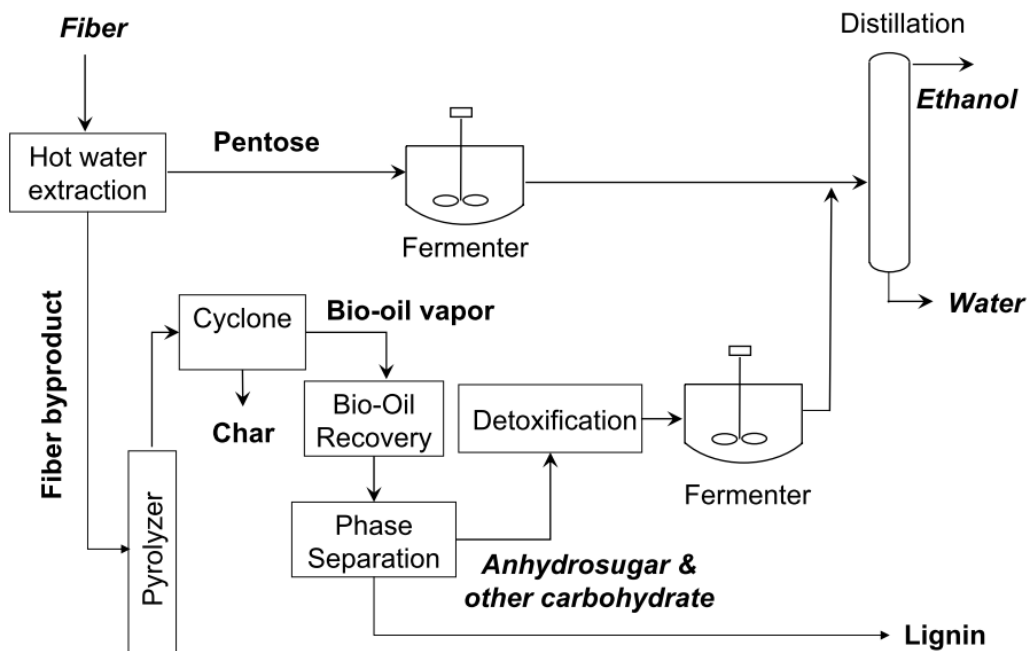


Figure 21: Bio-Oil Fermentation [106]



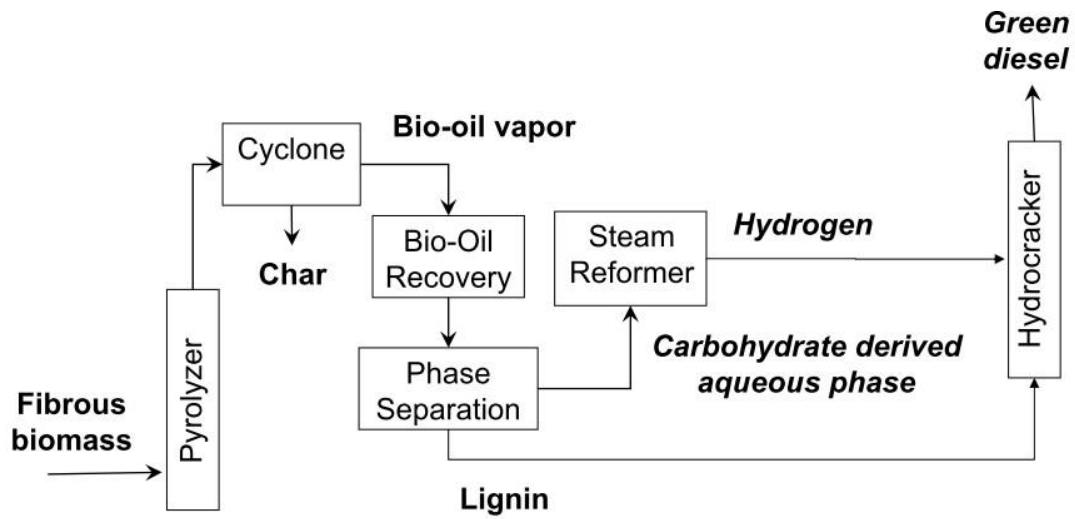


Figure 22: Bio-Oil Hydrocracking [106]

Since the different methods have now been discussed in order to produce potentially high quality oil in this chapter, the following chapter describes the measurement techniques, which can be employed to determine the quality of the oil output.

## **2.5 Measurement methods of Oil output**

As mentioned in chapter 1.1, the purpose of these experiments will be to optimise the pyrolysis parameters for the bio oil energy content. Consequently it is very important to choose the correct analysis methods to determine the oil parameters. There are numerous test, which can be conducted. The following methods are described in this chapter:

Calorific value (chapter 2.5.1)

- To determine the energy content of the oil.

Viscosity and stability of the oil, which also includes the following sub-tests (chapters 2.5.2 and 2.5.3)

- Thermogravimetry (TGA), which will determine the structure change of the oil over a period of time at different temperatures.
- PH, as acids will cause a viscosity shift during storage time
- Moisture which should not be too high, but also not under 10%, as it will result into a very high density and unstable oil [40].

Composition FTIR and GC-MS (chapter 2.5.4)

- The Fourier-transform infrared spectroscopy (FTIR) of the bio-crude provides insight of the oil quality in regard to HHV as well as impurities of the oil, as well as degradation by-products [120].
- Gas chromatography – mass spectrometry (GC-MS) This combined method is used to identify traces of substances in samples provided and thus, the overall oil composition can be determined via this method

### 2.5.1 Calorific value

The calorific value can be determined under either constant pressure or constant volume. Whereas the constant pressure method is the most affordable one. The bio oil can be analysed of its energy content via the calorimeter method by burning an amount of the fuel and capturing the heat released in a known mass of water, energy released by measuring the initial and final temperatures, can be calculated with:

$$H = \Delta t \cdot m \cdot C_p \quad (1)$$

, where H = heat energy absorbed (in J),  $\Delta t$  = change in temperature (in °C), m = mass (in g), and  $C_p$  = specific heat capacity (4.184 J / g • °C for water).

There are also various other measurement methods to determine the energy content of the oil [121]:

- ✓ DTA – Differential Thermal Analysis temperature difference (between sample and reference)
- ✓ DSC – Differential Scanning Calorimetry heat difference (between sample and reference) (Figure 23)
- ✓ TG - Thermogravimetry mass
- ✓ TMA – Thermomechanical Analysis dimensions
- ✓ Calorific bomb (Figure 24), which is a classic constant volume measurement method

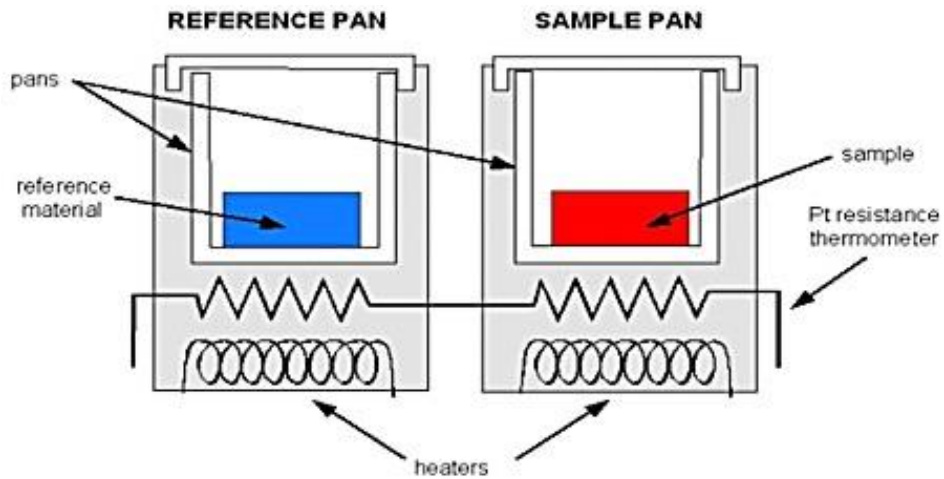


Figure 23: DSC measurement method [122]

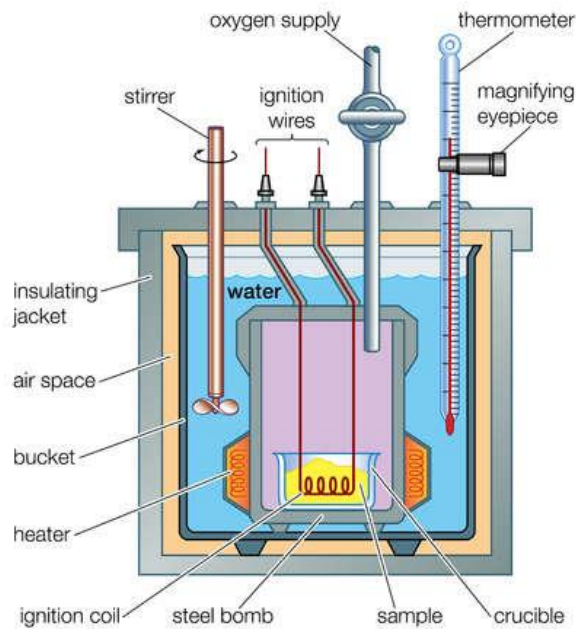


Figure 24: Calorific bomb [123]

## 2.5.2 Viscosity

The American Petroleum Institute (API) has a standardised measurement. The measured API gravity or degrees determine the density of the oil, the lower the API gravity of the hydrocarbon, the denser the oil [124] (Table 6).

Table 6: API and density comparison between Bitumen and light oil

Oil type	Light Oil	Bitumen
Combustion CO <sub>2</sub> (lbs/bbl)	926	1149
Oil Density (lbs/bbl)	298.6	354.1
API Gravity	34.2	8

### 2.5.3 pH measurements

pH measurements are normally determined by Total Base Number (TBN) and Total Acid Number (TAN) for the concentrations of the base content and the acid content of the oil, which are determined by ASTM D664-89 standard [125]. This measurement is necessary as the higher the acid concentration is, the higher is the number of hydrogen ions (H<sup>+</sup>) content of the oil which will result in acid corrosion and thus in unstable oil. Besides the traditional PH measurement methods with devices such as the Mettler DL25 titrator, there is an Australian Modified pH Test Method consisting of four steps [125]:

- 1) Into a clean, dry analysis cup weigh approximately 10g of sample.
- 2) Manually add 50mL of TAN solvent per ASTM D 664-89 (Isopropyl Alcohol, Toluene, & Water)
- 3) Mix by agitation & place cup under suitable glass pH electrode linked to a Denver Titrator (or equivalent).
- 4) After about 3 minutes read stabilized result as pH on titration controller screen.

## 2.5.4 FTIR and GC-MS

Fourier-transform infrared spectroscopy (FTIR) can be utilised to determine various functional groups within the oil such as O-H (alcohol), H<sub>2</sub>O, C=C (aromatics), different solubles and eluate [126]. The output graph with the different wavelengths on the x-axis and the amplitude, which determines the amount present in the sample, can be seen in Figure 25.

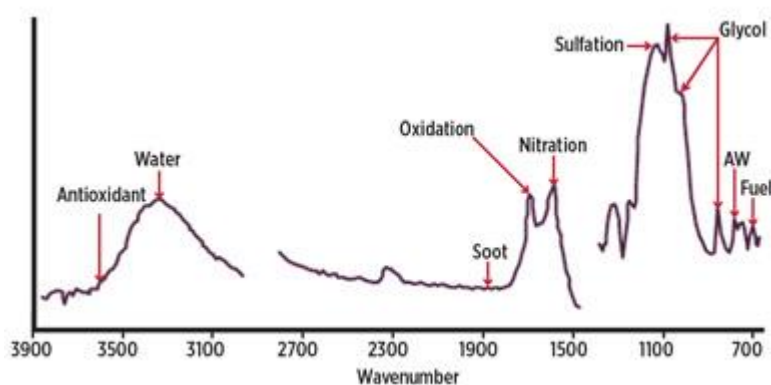


Figure 25: FTIR graph example [127]

For conducting the analysis, a sample is placed between an interferometer and a detector. The light source needs to uniformly emit all wave-lengths in the spectrum, so that the detector can record the amplitudes of the sample reflections. For each wavelength an interferogram (amplitude) is recorded and send to a PC to assemble the spectrum graph (Figure 26).

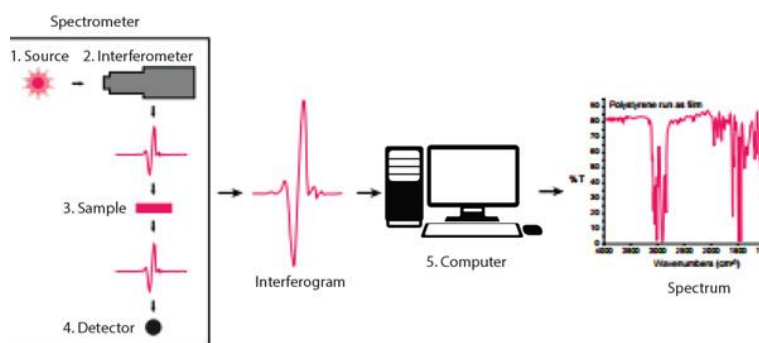


Figure 26: FTIR measurement method [127]

The gas chromatography – mass spectrometry (GC-MS) has been used since the late 1960s [128] and is one of the most substantial ways to analyse the material samples and the individual component. For this process, the oil is dissolved into an organic solvent which allows to identify and quantify the material samples. Figure 27 shows the inside of an GC-MS device. For the gas chromatography the dissolved sample will be injected into the column oven, where it is mixed with gas (He, N<sub>2</sub>, H<sub>2</sub>) and then transferred over the spectrometer column where the mixture can slow down and separate based on mass as well as volatility. This will then result into an ion-chromatogram to visualise different organic components. The mass spectrometry exposes the sample to ions to charge the particles, so that they can pass through the filter into the detector. The relationship between charge and mass will then be compared to a databased and determines the material composition.

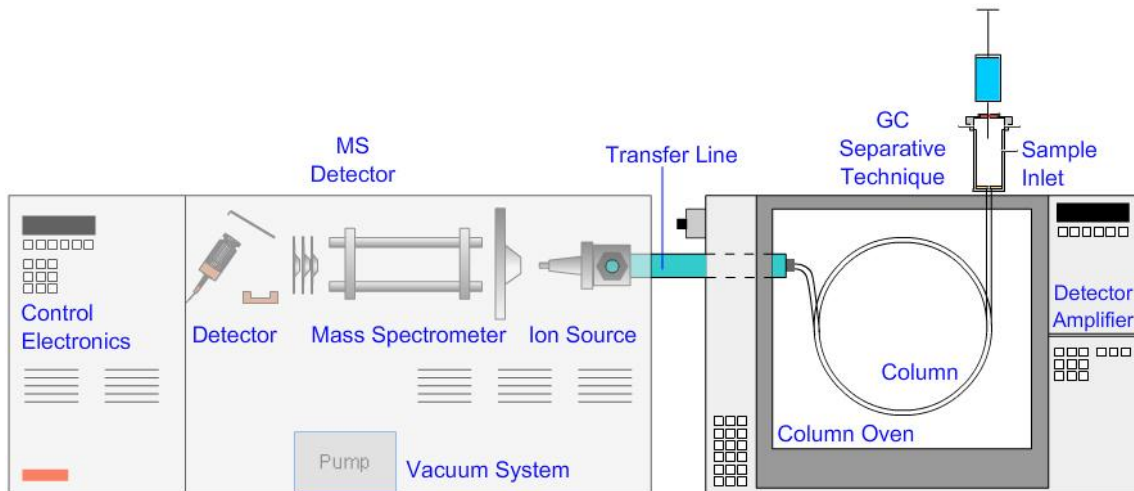


Figure 27: GC-MS setup [129]

## **3 Methodology**

### **3.1 Feedstock**

The sugarcane bagasse, which was provided by the the Sunshine Sugar Mill (Broadwater, New South Wales, Australia) was stored indoors throughout the experimental period. The bagasse was dried for 60 days in ambient condition. The material was not milled and contained various particle sizes. The chemical composition of sugarcane bagasse is presented in Table 8.

### **3.2 Pyrolysis Test Rig**

In this study, fixed bed reactor was used as the furnace heats up the small area very quickly and uniform heat distribution can be also realized within the fixed bed reactor with amount of feedstock. In addition to that, a fixed bed reactor is the most cost efficient solution. For the reactor, material must be chosen which does not react with the feedstock, vapour or heat. There are different options such as ceramic which is the most expensive solution, heat resistant glass or stainless steel. Stainless steel is relatively easy to form, it can be welded and is more affordable than the other two solutions; stainless steel is can be used for a large size application. For this experiment, a stainless steel tube is constructed for the introduction of a concept and included into this chapter. Initial experiments showed however same results by using the temperature range proposed in this research project and thus, for visibility reasons, a heat resistant glass container will be used for the execution of further experiments in regard to investigate the best temperature for the process.



### 3.2.1 Reactor design

The following equations are used to design the reactor size and how much feedstock can be processed as well as to calculate the reaction time of the of the pyrolysis process.

The steam was determined by:

$$Y = \frac{\sum_i 12W_p \alpha_i C_i}{W_f F_c} \quad (3)$$

Where  $W_p$  is the product per unit of time,  $\alpha_i$  is the number of carbon atoms in the component represented by the species  $i$ ,  $C_i$  is the mole fraction of  $i$  in the steam product,  $W_f$  is the feed inside the reactor in kg/s, and  $F_c$  is the carbon fraction. The carbon molecular weight is 12 kg/kmol.

The reaction rate was determined by the residence time  $\tau$ :

$$k_g = \frac{\ln(1 - X_c)}{\tau} \quad (4)$$

Carbon fraction  $X_c$  in the vapour stream was calculated by the final carbon fraction  $C$  and the initial  $C_0$ :

$$X_c = 1 - \frac{C}{C_0} \quad (5)$$

Chemical equations inside of the reactor are assumed to be homogenous due to good heat conductivity, and short connections between the reactor and the condensation train. The calculation can be processed with a stoichiometric equation with the species  $j$  over the reaction:

$$F_{jn} + G_j = F_{jn} + \frac{dN_j}{dt} \quad (6)$$

Where  $G_j$  is the rate of the species  $j$  formed inside the reactor. Furthermore we can say that:

$$G_j = \int_{V_R} dG_j = \int_{V_R} r_j dV \quad (7)$$

For a packed bed reactor we can add the following volume time dependency for  $r_j$ :

$$r_j = (r_j)_v = \frac{1}{V} \frac{dN_j}{dt} \quad (8)$$

The design equation for the  $m^{\text{th}}$  independent reaction was calculated as:

$$\frac{dZ_m}{d\tau} = r_m + \sum_k^{np} (\alpha_{km} r_k) \left( \frac{t_{cr}}{c_0} \right) \quad (9)$$

Where  $C_0$  is the concentration of the selected reference stream  $F_{tot}$  and:

$$Z_m = \frac{X_m}{(F_{tot})_0} \quad (10)$$

With the reaction time  $t_{cr}$  also freely selected:

$$\tau = \frac{V_r}{u_0 t_{cr}} = \frac{t_{sp}}{t_{cr}} \quad (11)$$

With the molar flow rate  $j$  and the volumetric flow rate  $v$ , the concentration of the conveniently selected reference stream can be defined by:

$$C_j = \frac{j}{v} \quad (12)$$

When the input stream is equal the reference stream:

$$C_j = \frac{(F_{\text{tot}})_0}{v} \left( v_{j0} + \sum_m^{nj} (s_j)_m Z_m \right) = C_0 \left( v_{j0} + \sum_m^{nj} (s_j)_m Z_m \right) \quad (13)$$

It can be assumed, that the density is almost constant:

$$v_{\text{in}} = v \quad (14)$$

For the  $i^{\text{th}}$  chemical reaction:

$$r_i = k_i(T_0) e^{\frac{\gamma(\theta-1)}{\theta}} \cdot h_i C_j^s \quad (15)$$

Where  $h_i C_j^s$  the function of species concentration,  $\gamma$  is the activation energy and  $k_i(T_0)$  can be taken as the reaction rate is assumed to be constant with sufficient feed stock, constant heat supply, and stable gas concentration. Furthermore we can conclude that:

$$C_j = \frac{(F_{\text{tot}})_0}{v} \left\{ \frac{(F_{\text{tot}})}{(F_{\text{tot}})_0} \gamma_{jn} + \sum_m^{nj} (s_j)_m Z_m \right\} \quad (16)$$

, where energy  $\gamma$  is constant:

$$\gamma_{jn} = \gamma_{j0} \quad (17)$$

For the gas phase reaction, which means that the flow rate  $F$ , temperature  $T$  and pressure  $P$  is molar:

$$v = v_0 \frac{(F_{\text{tot}})}{(F_{\text{tot}})_0} \frac{T}{T_0} \frac{P_0}{P} \quad (18)$$

Previous studies reported that high oil output were obtained between 450 °C and 550 °C [130]. At temperatures higher than 550 °C, secondary reactions of volatiles led to a significant lower bio-oil yield. However, quality of oil was reported to be better because of the lower residence times, which was shown with various feedstocks including sugarcane bagasse [96, 131-137].

Based on the above calculations, the following process conditions were used for the study:

Particle sizes of the feedstock are in between 0.2 and 1mm, while the moisture content was 15%. The Reactor pressure was calculated to vary from 1.6atm for 300°C to 3.3atm for the highest temperature of 600°C. The maximum temperature and heating rates are calculated and can be seen in Table 7.

Table 7: Reactor parameters of maximum temperature, heating rate and calculated time until maximum temperature is reached

Temperature °C	Heating rate K/s	Time until max temp. in sec.
300	10	33.00
300	20	16.50
300	30	11.00
300	40	8.25
400	10	38.00
400	20	19.00
400	30	12.67
400	40	9.50
450	10	43.00
450	20	21.50
450	30	14.33
450	40	10.75
500	10	48.00
500	20	24.00
500	30	16.00
500	40	12.00
550	10	53.00
550	20	26.50
550	30	17.67
550	40	13.25
600	10	58.00
600	20	29.00
600	30	19.33
600	40	14.50

### **3.3 Reactor Operation**

The pyrolysis reactor consists of a 150 ml glass Erlenmeyer flask fitted with 2 or 3 holed glass stopper. The reactor setup is shown in Figure 28. The reactor was connected to a condensation train and a vacuum system. As the initial heating source was insufficient, fire heating was used as heat source for the rest of the experiments. The pipes leading from the reactor to the condensation train are short enough to limit condensation before the traps. The condensation system consists of running tap water, which removed the organic vapours and gas products from the reactor through the condensation train (Figure 28). The condensable gases were then condensed in the traps and recovered as liquid in a glass beaker (100 ml). The produced liquid was later weighed and analysed.

In the pre-testing runs, it was shown that the fastest heating ramp was achieved with the lowest residual times for the oil within the reactor (data not shown). Therefore, the pyrolysis reactor was heated as per the designed heating rate of 40 K/sec, residence time of 20 min and final pyrolysis temperature (300, 400, 450, 500, 550 and 600 °C). The best temperature range was investigated in the second part of the experiment, when the reactor was operated at 300 °C to 600 °C. Each process condition was repeated several times and two runs were carried out for each studied temperature. In the end, 4 temperatures were selected and ranged from 400-550 °C.

Upon completion of experimental run, the reactor and the condensation train were allowed to cool under atmospheric pressure until the sample temperature was below 120°C. The sample holder was then removed and weighed, after which the residue (charcoal) was removed and stored for analysis. A typical run would take between 45 to 60 min, after which the reactor was allowed to cool for 1 h depending on the pyrolysis temperature employed.



Figure 28: Experimental set-up showing the glass pyrolysis reactor, electric heating system, condensation train, gas sampling, oil collection and vacuum cooling system.

The experiment was carried out in a controlled environment in fume hood.

### 3.4 Analyses

The moisture and dry matter content were determined by drying a known amount (6.5 g) of bagasse at 105 °C to constant weight [138]. Ash content was determined by igniting the dried samples in a muffle furnace at 550°C for 1 hr and weighing the residue after a cooling period at room temperature in a dessicator [138]. The pH level of the feedstock was determined by a pH meter (Metrohm pH meter). A calorific and FTIR analysis provides insight of the oil quality in regards to HHV as well as impurities of the oil [120].

Fourier-transform infrared spectroscopy (FTIR) analyses of the bio-crude were performed on a Nicolet 870 Nexus FTIR spectrometer equipped with a Smart Endurance single bounce diamond attenuated total reflectance (ATR) accessory (Nicolet Instrument Corp., US) as described elsewhere [139]. The spectrometer incorporated a

KBr beam splitter and a deuterated triglycine sulfate room temperature detector. Spectra were collected from 4000 cm<sup>-1</sup> to 525 cm<sup>-1</sup> using 64 scans at 4 cm<sup>-1</sup> resolution and a mirror velocity of 0.6329 cm s<sup>-1</sup>. The measurement time for each spectrum was ~60 s.

The organic/oil phase samples were analysed by Gas chromatography–mass spectrometry using an Agilent 6890 Series Gas Chromatograph and a HP 5973 mass spectrometer detector, employing helium as the carrier gas [140] using an Agilent 6890 Series Gas Chromatograph and a HP 5973 mass spectrometer detector, employing helium as the carrier gas. The installed column was an Agilent HP-1, 30 m x 0.25 mm x 0.25 µm. Samples were injected with a split ratio of 10:1 into the injection port set at 230 °C. The temperature program commenced at 90 °C held for 10 min then heated at a rate of 3 °C.min<sup>-1</sup> to a temperature of 260 °C. Once the temperature was reached the column was then held for another 5 min. Compounds were identified by means of the Wiley library-HP G1035A and NIST library of mass spectra and subsets-HP G1033A (a criteria quality value >80% was used). Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) for the detection and quantification of trace and heavy metals was carried out as described in [141]. Biomass compositional (cellulose, hemicelluloses, lignin and ash) analysis of the bagasse and char solid samples were analysed according to the standard methods developed by National Renewable Energy Laboratory (NREL), USA [142]. Elemental analyses such as carbon, hydrogen, nitrogen, sulphur and oxygen content of the sugarcane bagasse and char were determined by using a Flash EA 1112 Organic Analyser (Thermo Scientific, US) [139]. Briefly, Samples of biochar and bagasse were dried overnight at 105 °C to constant weight prior to analysis. A subsample of dried char or bagasse (2 – 4 mg) was encapsulated in a tin container for the measurement of carbon, hydrogen and nitrogen while another subsample was encapsulated in a silver container for analysis of oxygen content. The higher heating value (HHV) of the bagasse and char samples were calculated based on the following equation [143]:

$$HHV \left( \frac{MJ}{kg} \right) = - 1.3675 + 0.3137 \times Carbon + 0.7009 \times Hydrogen \\ + 0.0318 \times Oxygen$$



### 3.4.1 Mass Balance

During pyrolysis, biomass undergoes a process that yields gas, liquid and solid products. The product fractions were estimated from literature to be 0.65, 0.2 and 0.15 for oil, char and gas respectively. Nitrogen is inert and is not produced by the pyrolysis reaction. Therefore, inlet and outlet mass flow rates of nitrogen are equal.

$$\text{Bagasse mass (M}_{\text{bagasse}}) + \text{Mass of nitrogen (M}_{\text{nitrogen}}) = \text{M}_{\text{nitrogen}} + \text{Mass of syngas (M}_{\text{gas}}) + \text{Mass of bio-oil (M}_{\text{oil}}) + \text{Mass of biochar (M}_{\text{biochar}})$$

$$\text{as } N_2 \text{ IN} = N_2 \text{ OUT}$$

Which then results into,

$$M_{\text{bagasse}} = M_{\text{gas}} + M_{\text{oil}} + M_{\text{biochar}}$$

### 3.4.2 Energy balance

The energy balance for each temperature was calculate as the energy in ( $Q_{\text{in}}$ ) and energy out ( $Q_{\text{out}}$ ). As,  $N_2$  gas does not undergo any phase change or reaction during the process and it requires heating and cooling to the design temperatures. On the other hand, biomass requires heating, and then undergoes a reaction resulting in phase change. The produced pyrolysis products requires cooling and condensation as well.

$$Q_{\text{out}} = Q_{\text{in}} + Q_{\text{generated}} - Q_{\text{consumed}} - Q_{\text{accumulated}} + Q_{\text{losses}}$$

The ratio between the weight of solids collected in the reactor ( $Y_{\text{char}}$ , wt.%), the weight of tarry phase ( $Y_{\text{oil}}$ , wt.%) collected from the condenser train at room temperature and the weight of (dry) bagasse ( $Y_{\text{bagasse}}$  wt.%) introduced into the system. The response,  $Y_{\text{gas}}$ , was not considered in this study due to the large deviation due to the presence of losses.

## 4 Results and Discussion

### 4.1 Effect of pyrolysis temperature (300°C to 600°C) on chemical composition of sugarcane bagasse

Table 8 presents the major chemical and physical composition of the bagasse used. The bagasse received in the laboratory had a particle size between 0.2 to 1 mm and contained 23.6% of moisture. The moisture content was then lowered to 15 % under room temperature prior to the experimental runs. Elemental analysis showed that the composition of the bagasse used in the present experiment is close to general elemental composition of bagasse reported in the literature. However, the ash content is quite high at 15.6 wt.% [144]. As ash contains the inorganic components e.g. metal oxides, pyrolysis temperature and residence time may lead to different yields of products and contaminate products. The amount and/or distribution of pyrolysis products viz., biochar, bio-oil and gas is heavily dependent on the initial composition of biomass. In Table xx, cellulose, hemi-cellulose and lignin fractions for bagasse were presented. Results show that glucan content in bagasse was twice the concentration of xylan. The initial heating value of bagasse was 17 MJ/kg.

Table 8: Chemical composition of the sugarcane bagasse

Parameter	Sugarcane bagasse
Dry matter (%)	76.4
Organic matter (dry wt, %)	84.4
Moisture content (%)	23.6
Ash content (dry wt, %)	15.6
C (g/kg)	403.5
N (g/kg)	2.6
Glucan (dry wt, %)	37.5
Xylan (dry wt, %)	17.9
Galactan (dry wt, %)	1.5
Arabinan (dry wt, %)	2.5
Lignin (dry wt, %)	30.2

Elemental composition of bio-char and oil resulting from pyrolysis of sugarcane bagasse at 300 °C, 400 °C, 500 °C and 600 °C is presented in Table 9. As expected, the ultimate analyses showed that the carbon content in biochar increased at first from 300°C to 500 °C and then decreased with an increase in pyrolysis temperature to 600°C. A similar trend was also noticed with hydrogen and C/O molar ratio. However, C/H molar ratio did not follow any trend. The possible reason for this discrepancy could be the generation of more thermostable compounds e.g. benzene at 600 °C through condensation and polymerisation of volatiles at higher temperature. During the experimental run, volatile compounds were released and were absorbed in the condensation train; however, some of the residuals were entrapped in the biochar. With respect to the HHV, the highest HHV of the biochar was obtained at pyrolysis temperature of 400 – 500 °C (Table 10). On the other hand, the highest HHV for bio-oil was 300 °C, however, it can be seen that the Hydrogen and Carbon levels for 300 °C are the lowest and the Oxygen level the highest, as expected due to the lower temperature. However, the quantity of gas was very high at 300°C followed by at 500-600 °C. As expected, the ultimate analyses showed that the carbon content in oil was highest at 300 °C followed by at 500 °C and 600 °C. A similar trend was also noticed with H. However, highest C/H and C/O molar ratio were noticed at 600 °C. It should be noted that biochar samples at all temperatures had lower C/H and C/O ratios than the untreated sugarcane bagasse indicating the preferential elimination of O and H relative to C in volatile matter. These results are in agreement with the results obtained by Crombie et al. [145]. In the above study, researchers have reported that small changes in H content in the biochar had a proportionally larger effect on C/H molar ratio than the respective changes in O. Both ratios decreased in biochar with increasing pyrolysis temperature. The increase in C/H ration with increase in temperature indicates that highest stable bio-oil was obtained at 600 °C.

Table 9: Elemental composition, C/H, C/O and calorific heating value (mf basis) of biochar and oil obtained during pyrolysis of sugarcane at 300-600 °C.

<b>Biochar</b>								
Max. Temp	Nitrogen	Carbon	Hydrogen	Sulphur	Oxygen	C/H molar ratio	C/O molar ratio	HHV (MJ/kg)
<b>300 °C</b>	0.00	15.25	8.91	0.00	58.72	1.71	0.26	9.19
<b>400 °C</b>	0.00	19.08	9.06	0.00	53.49	2.11	0.37	11.29
<b>500 °C</b>	0.00	19.31	9.60	0.00	55.48	2.01	0.34	11.78
<b>600 °C</b>	0.00	19.18	9.16	0.00	69.46	2.09	0.27	9.67
<b>Oil</b>								
Max. Temp	Nitrogen	Carbon	Hydrogen	Sulphur	Oxygen	C/H molar ratio	C/O molar ratio	HHV (MJ/kg)
<b>300 °C</b>	0.00	65.79	3.45	0.00	11.06	19.07	5.95	25.91
<b>400 °C</b>	0.52	56.53	3.06	0.00	11.59	18.47	4.88	22.47
<b>500 °C</b>	0.54	63.06	3.30	0.00	12.04	19.11	5.24	25.01
<b>600 °C</b>	0.50	59.95	2.53	0.00	6.43	23.66	9.32	23.62

The yields of biochar, oil and gas obtained from each pyrolysis experimental run are presented in Table 10. Results show that temperature had a profound effect on pyrolysis yields and quality at the tested temperature ranges (300 °C to 600 °C). Biochar yields decreased with increase in temperature from 300 °C to 600 °C with the highest yield obtained at 300 °C. The lower biochar yields obtained at higher temperatures is attributed to the fact that at higher temperature greater decomposition of organic material takes place promoting the release of volatile material [145]. By increasing the pyrolysis temperature from 300 to 600 C, a higher percentage of bio-oil and gas was obtained. These results are in accordance with previous results indicating that increased char devolatilization at higher temperature will result in a higher yield of liquid and gaseous products [145]. Both these results suggest that the amount and type of volatile material produced during the tested temperature range can result in the degree of breakdown of cellulose, hemicellulose and lignin [146].

Table 10: Mass balance average of Sugarcane Bagasse Pyrolysis

Temperature	Feedstock (g)	Char (g)	Char (%)	Oil (g)	Oil (%)	Gas (g)	Gas (%)
300 °C	6.620	3.54	53.54	0.91	13.76	2.18	32.87
400 °C	6.582	2.40	36.48	2.79	42.43	1.32	20.09
500 °C	6.584	2.20	33.45	3.73	56.63	0.64	9.65
600 °C	6.622	2.26	34.15	3.47	52.39	0.88	13.33

A close observation of the FTIR spectra in Figure 29, reveal a vast difference in the amount of aromatics produced during the pyrolysis process. This was seen as an increase in the peak at the frequency of  $1512\text{ cm}^{-1}$  and at  $833\text{ cm}^{-1}$ . These long molecule chains will cause the potential fuel to be unstable and break down in a very short time [103-105]. However, it can also be seen that there is a high content of ethers and other alcohols as shown by vibrations at peak  $1215\text{ cm}^{-1}$ , which are promising as a potential fuel source. As the samples were not stripped of water, a peak at a frequency of  $3335\text{ cm}^{-1}$  can be seen, which is not of concern once the fuel would be treated. Furthermore, a relatively high amount of alkanes ( $1454\text{ cm}^{-1}$ ,  $1378\text{ cm}^{-1}$ , and  $1362\text{ cm}^{-1}$ ) as well as alkenes ( $1605\text{ cm}^{-1}$ ,  $1594\text{ cm}^{-1}$ ) can be seen. These compounds could be reported to cause deposition of solids in combustion turbine as well as engines and thus consequently damage the machines permanently. Nevertheless, the relationship of alcohols and volatile substances is shown. Individual components at different wavelengths can also be seen in Appendix 8.3.

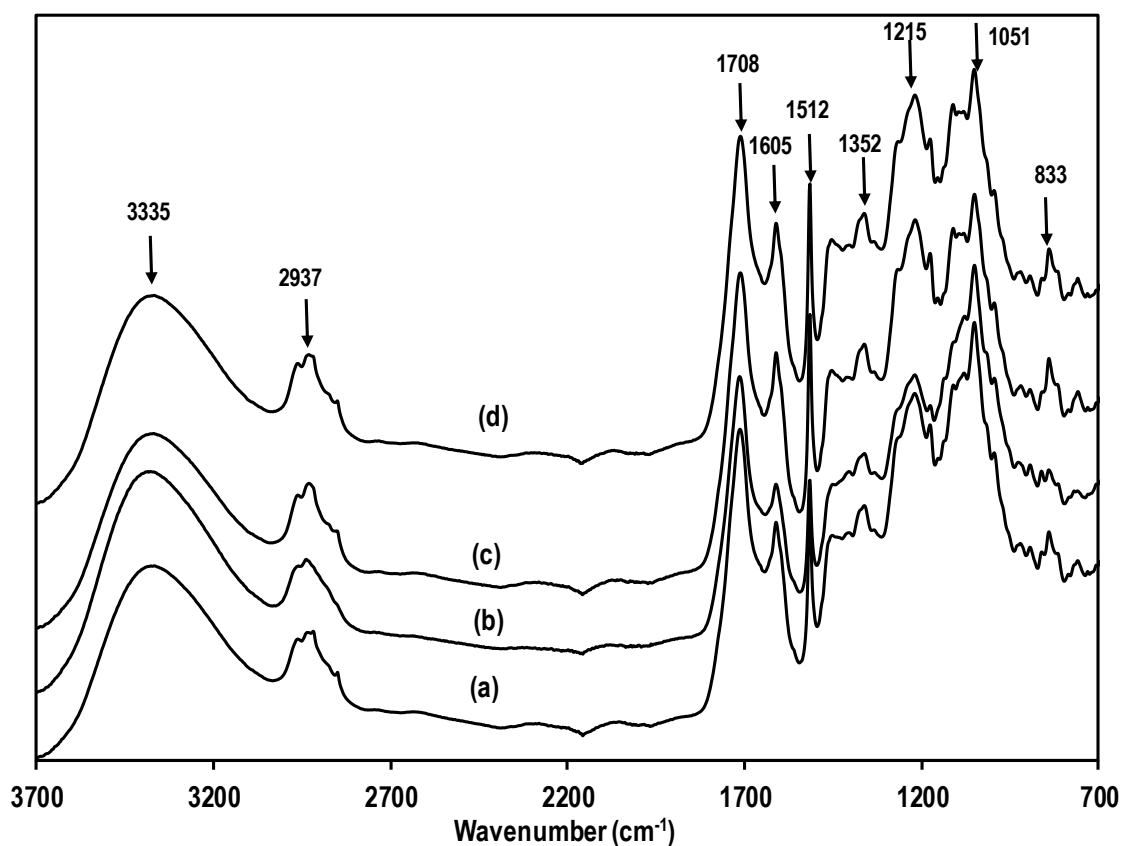


Figure 29: FTIR spectra of oil obtained during the pyrolysis of sugarcane bagasse at a) 300 °C, b) 400 °C, c) 500 °C, and d) 600 °C

#### 4.1.1 Effect of temperature range of 450 °C to 550 °C on bio-oil quality

In the second phase of the experiment, pyrolysis temperatures were narrowed down to 450°C, 500°C, and 550°C. The ultimate analyses, C/H molar ratio and C/O molar ratio along with HHV values are presented in Table 11. Prior to the analyses, samples were stripped off the H<sub>2</sub>O content. Pyrolysis temperature had profound influence on the HHV values and the values obtained in the second phase of the experiment were lower than those obtained at 500 °C in the preliminary experiments (Table 11). HHV values increased with increase in pyrolysis temperature. The highest HHV value of 25.54MJ/kg was obtained at 550°C and it was expected as the oxygen content was low with slightly higher values for H and C than at 450°C and 500°C. Previous studies

reported that high oil yield were obtained between 450°C and 550°C [130]. At temperatures higher than 550°C, secondary reactions of volatiles led to a significant lower bio-oil yield. However, quality of oil was reported to be better because of the lower residence times, which was shown with various feedstocks including sugarcane bagasse [96, 131-137].

Table 11: Elemental composition, C/H, C/O and calorific heating value (mf basis) of bio-oil obtained during pyrolysis of sugarcane at 450-550 °C

Sample	Nitrogen	Carbon	Hydrogen	Sulphur	Oxygen	C/H molar ratio	C/O molar ratio	HHV (MJ/kg)
450 °C	0.00	56.30	6.46	0.00	37.25	8.72	1.51	23.35
500 °C	0.00	56.08	6.40	0.00	37.53	8.76	1.49	24.85
550 °C	0.00	57.02	6.44	0.00	36.55	8.85	1.56	25.54

The FTIR spectrum for temperature 450-550 °C is presented in Figure 30. Temperature had a profound influence on the production of alcohols and alkenes. Very high content of ethers and other alcohols were noticed at vibrations 1232 cm<sup>-1</sup> and 1159 cm<sup>-1</sup>. Similarly, alkenes were visible at wavelength 2966 cm<sup>-1</sup>, 2937 cm<sup>-1</sup>, 2849 cm<sup>-1</sup>, 1558 cm<sup>-1</sup>, and 1435 cm<sup>-1</sup>. Interestingly, aromatics were completely absent in all samples indicating very high and long-term stability of the bio-oil. Details of the individual components at different wave lengths are presented in Appendix 8.3. Furthermore, no wax deposits, due to possible aromatics compounds, were noticed even after the analysis was repeated four months after the experiments. Similar results were also obtained with respect to HHV as well as the FTIR spectra of oil.

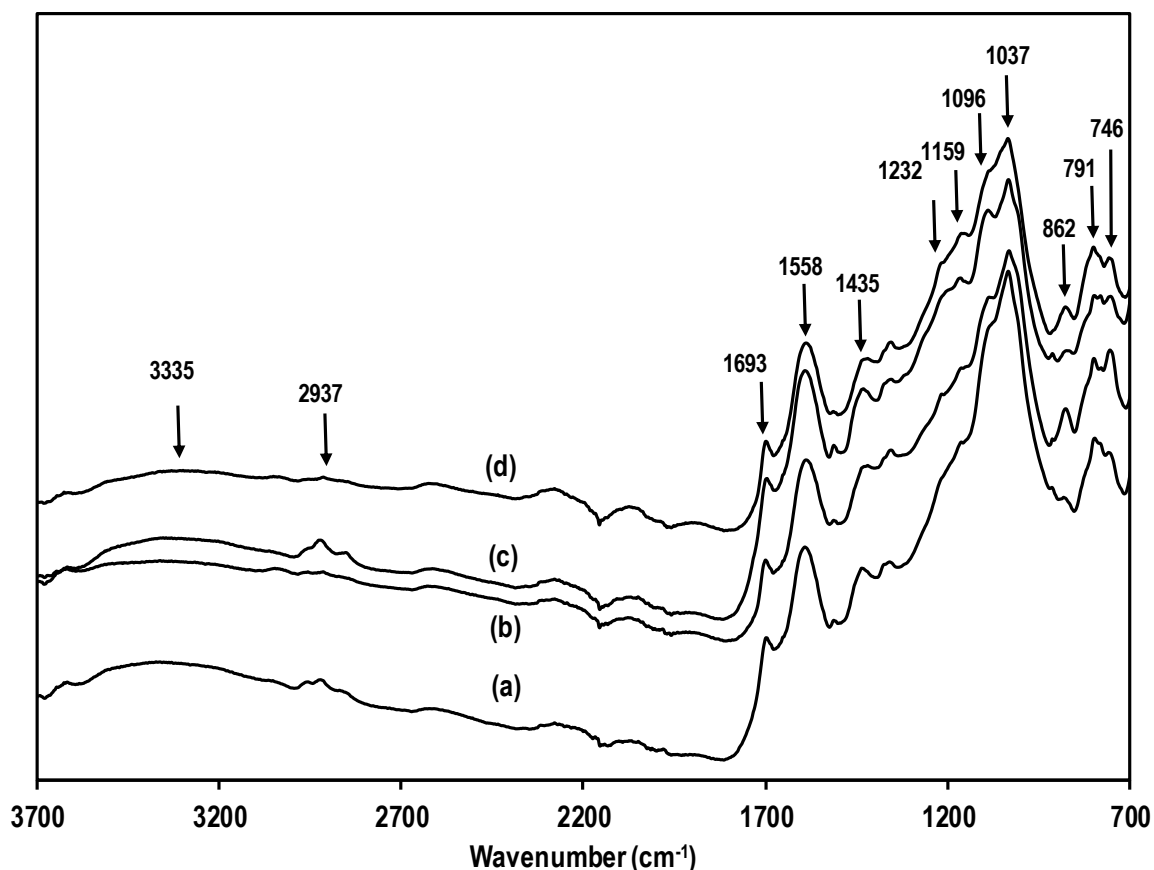
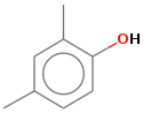

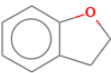
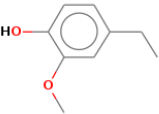
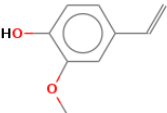
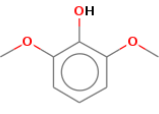

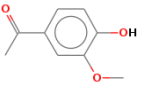
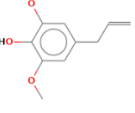
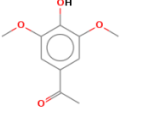
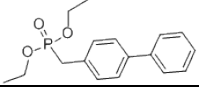


Figure 30: FTIR spectra of oil obtained during the pyrolysis of sugarcane bagasse: a) Reference curve from worst previous sample, b) 450 °C, c) 500 °C, and d) 550 °C

Mass balance of the pyrolysis products obtained at 450 °C to 550 °C is presented in Table 13, It can be seen that the values are comparable with the values found in the literature [99]. Oil yields decreased with increase in pyrolysis temperature from 450 °C to 550 °C. At 550 °C, oil yields were decreased by 6.4%, but at the same time its HHV was increased by 11%. Moreover, the long term storage stability of the oil, which is dependent on the O content, has improved (Table 9 and Table 11). Thus, less energy is required for downstream processing of the fuel. Preliminary results showed that a mass loading up to the maximum, for the reactor size, led no variation in the percentage of char yields, as well as no variations in the oil content for these experimental conditions.



Table 12: Composition analysis of solid output for narrowed down temperature range

Compounds	Chemical structure	450 °C (area %)	500 °C (area %)	550 °C (area %)
2,4-dimethyl phenol		3.20	0.54	2.41
4-ethyl phenol		25.42	18.78	19.83
2,3-dihydro-benzofuran		16.23	19.37	19.62
4-ethyl-2-methoxy-phenol		5.70	3.29	6.03
2-methoxy-4-vinylphenol		7.97	5.69	8.41
2,6-dimethoxy-phenol		4.77	3.44	4.01
Vanillin		3.01	0.00	0.00
Apocynin		0.07	0.00	0.00
2,6-dimethoxy-4-(2-propenyl)-phenol		2.61	4.49	4.21
Ethanon, 1-(4-hydroxy-3,5-dimethoxyphenyl)-		0.91	2.25	2.34
Diethyl (4-biphenylmethyl)phosphonate		0.00	0.08	0.00
2- (octyloxylcarbonyl) benzoic acid		0.00	0.17	0.15

The chemical composition of the biochar at the three studied temperatures is presented in Table 12. Results showed that temperature had a profound effect on the type and

amount of chemicals produced at each pyrolysis temperature. The major chemicals produced include phenols, vanillin and benzoic acid. Based on the results, it can be suggested that the pyrolysis reactor has to be operated at the desired temperature and heating rate in order to repeat the experiments. Furthermore, the variation in bio-oil and char yield obtained during the process may depend on the contact between the sample and the hot zone especially for larger feedstock. Less contact between the feedstock and heating source may result in temperature gradients and incomplete reactions. Finally, loss of gases from the reactor, and changes in the feedstock character e.g. moisture content between runs may have also led to variation in the yield. These possible experimental errors were addressed in subsequent experiments. The accuracy of the oil yield was further improved by avoiding condensation in the pipes. The analysis of the solids were conducted as well and the results are shown in appendix 8.3. However, since this thesis is focused on the oil quality, the char analysis is not further elaborated on.

Table 13: Mass balance average of Sugarcane Bagasse Pyrolysis

<b>Temperature</b>	<b>Feedstock (g)</b>	<b>Char (g)</b>	<b>Char (%)</b>	<b>Oil (g)</b>	<b>Oil (%)</b>	<b>Gas (g)</b>	<b>Gas (%)</b>
<b>450°C</b>	6.550	2.175	33.206	3.971	60.623	0.404	6.171
<b>500°C</b>	6.610	2.181	32.995	3.869	58.539	0.560	8.465
<b>550°C</b>	6.662	2.136	32.062	3.717	55.801	0.809	12.137

The best oil output and yield was obtained at 550 °C. Input energy  $Q_{in}$  and output energy of the oil  $Q_{out}$  were used to estimate the energy balance and the results are presented in Table 14. Based on the energy balance, pyrolysis of sugarcane bagasse was optimal at 450 °C. Although the oil quality as well as yield obtained at 550 °C was higher than at 450 °C, the input energy needed to for the process was much higher at 550 °C than at 450 °C. Thus, taking into account the overall energy and mass balance, the optimal temperature to carryout pyrolysis of sugarcane bagasse is 450 °C.

Table 14: Energy balance for the pyrolysis process at the studied temperatures based on the oil HHV.

<b>Temperature</b>	<b>Q<sub>in</sub> (J/s)</b>	<b>Q<sub>out</sub> (J/s)</b>	<b>Efficiency in %</b>
<b>300°C</b>	61158.276	21391.296	34.98
<b>400°C</b>	83237.076	57209.519	68.73
<b>450°C</b>	94276.476	84915.655	<b>90.07</b>
<b>500°C</b>	105315.876	87843.623	83.41
<b>550°C</b>	116355.276	85493.415	73.48
<b>600°C</b>	127394.676	74259.8628	58.29

## 4.2 Further Concept Work

### 4.2.1 Stainless steel reactor design concept

As mentioned before, a steel tube reactor was compared to a glass reactor at the same temperature range. Both setups showed the same results in regard to the output. However, the concept of the design is showed in this sub-chapter.

To use a tube furnace, the following reactor was designed (Figure 31) which can fulfil the requirements in this project. The furnace has a diameter of 60mm and a length of 600mm. The stainless steel inlet, which forms the reactor tube has a wall thickness of 2mm would go into the heating zone (Figure 32), between 240mm and 360mm and will be longer than the furnace of about 50mm to allow space for the gas inlet and the condensed vapour output.

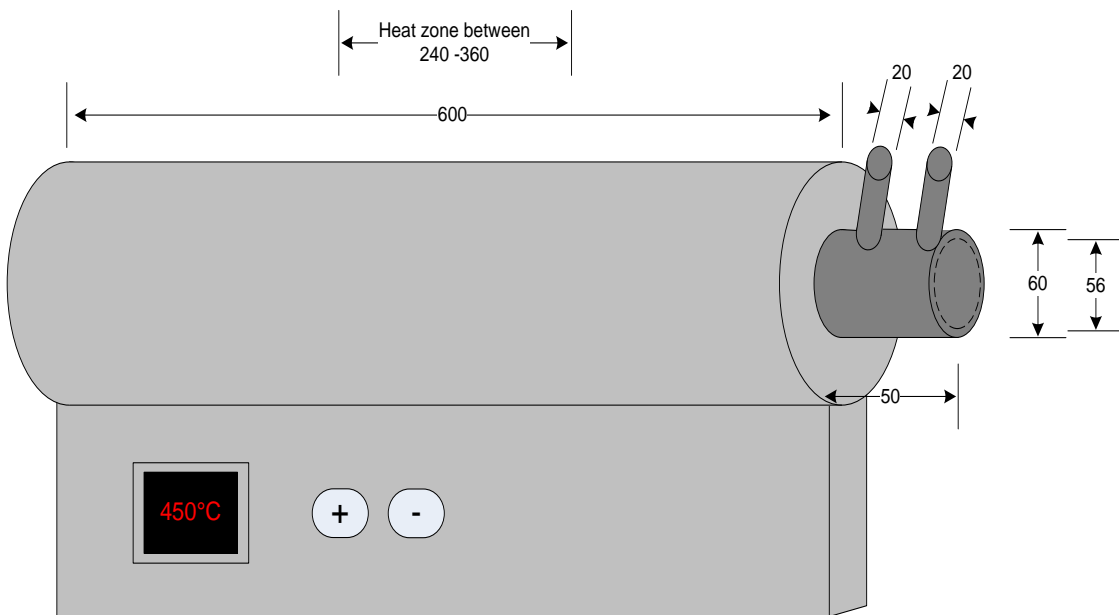


Figure 31: Steel reactor concept set-up



Figure 32: Steel reactor tube inlet

The volume needs to be calculated to determine the maximum feed stock, flooding of the reactor with Nitrogen etc.

$$A = \pi \cdot 28^2 \approx 2.5 \cdot 10^{-3} m^2$$

$$V = 2.5 \cdot 10^{-3} m^2 \cdot l = 2.5 \cdot 10^{-3} m^2 \cdot 0.36 m = 0.9 \cdot 10^{-3} m^3 \rightarrow \sim 0.9 l$$

#### 4.2.2 Choosing of a potential catalyst

As discussed in chapter 2.4.1, a catalyst should be used if the experiment is scaled up and thus the amount of feedstock is significantly larger than in this experiment. In order to improve heat conduction, metal balls can be used in between the feedstock to increase the chemical reaction rate [147]. There are two options of metals, which can be used:

- 1) Noble metals, which will provide a high activity, but will also be cost intense
- 2) Less cost intensive transition metals, which will however have a lower activity and are prone to deactivation

16Ni2Cu and 13.8Ni6.83Cu are found to be the most active metal alloys in regard to the hydrogenation activities, but have shown dissolution and recrystallization during the pyrolysis process [148]. However, using of a catalyst will increase the costs and thus no catalyst will be used in this research project.

## 5 Conclusion

This Master research project successfully investigated the optimum temperature of the pyrolysis oil output and showed that the HHV as well as the yield output at 550°C is the best amongst the investigated temperatures. The overall setup was made as simple as possible to achieve a realistic picture and open the possibility of making a promising technology suitable for the mainstream market. It was noted that an increase of the HHV of up to 11% is possible. The absence of Aromatics such as Vanillin and Apocynin in the oils enables longer storage times without risking the fuel to become unstable and forming solid deposits, even without post-treatment. Furthermore, the absence of aromatic components at the optimised temperature range would even enable the use in modern engines and turbines.

However, by paying attention to the energy balance it can clearly be seen that the pyrolysis process at 450°C is the most efficient way to produce bio-oil out of sugarcane bagasse. At this temperature the amount of aromatics is still low, but the yield as well as the HHV in comparison to the best oil at 550°C is much lower. The recommendation would be; In order to achieve the best oil, it is advised to use 550°C for the pyrolysis process, for an efficiency drop of approximately 17%. However, if the focus is on the best energy balance, using a maximum temperature of 450°C for the pyrolysis process provides the best solution. Overall the research project fulfilled all the aims and showed one step further into the direction of better utilisation of bio waste for energy harvesting.

### **Published work from this research:**

Sascha Stegen, “Investigation of oil quality output of a traditional pyrolysis process”, Bioenergy Australia Conference 2016, Queensland, 14-16 November 2016

To be submitted:

Sascha, S., Moghaddam, L., Doherty, B., Sunil, H. and Kaparaju, P., “ Pyrolysis Temperature Optimization of sugarcane bagasse to increase oil quality output“, Journal of Analytical and Applied Pyrolysis, Elsevier 2018

## 6 Future work

Although the temperature for the best quality of oil and the oil for the best energy balance for this research project was determined, the feedstock was relatively small. If the amount of feedstock increases it must be insured that the maximum heat ramp can reach the feedstock fast enough as it did with the small feedstock. Thus, this thesis contains a short elaboration on possible catalysts in chapter 4.2.2 for this case. Furthermore, sugarcane bagasse poses a very good feedstock for this investigation due to the amount which is produced in many countries world-wide. However, also other feedstock could be investigated under the same conditions and compared to the results presented in this thesis.

## 7 References and Appendices

### References

- [1] W. E. COUNCIL, "World Energy Resources Bioenergy 2016," 2016.
- [2] A. Lang, H. Kopetz, A. Stranieri, and A. Parker, *Australia's Under-Utilised Bioenergy Resources* vol. 1: Springer, 2013.
- [3] H. Wang, J. Male, and Y. Wang, "Recent Advances in Hydrotreating of Pyrolysis Bio-Oil and Its Oxygen-Containing Model Compounds," *ACS Catalysis*, pp. 1047–1070, 9 April 2013 2013.
- [4] A. E. Hanandeh, "Carbon abatement via treating the solid waste from the Australian olive industry in mobile pyrolysis units: LCA with uncertainty analysis," *Sage Waste Management and Research*, vol. 31, p. 12, 2013.
- [5] M. Sugar. (2017). Available: <https://www.msfsugar.com.au/the-industry/manufacturing-sugar/>
- [6] E. a. E. BDA Group. (2009). *The full cost of landfill disposal in Australia*.
- [7] M. Abu-Zreig and M. Al-Widyan, "Influence of olive mills solid waste on soil hydraulic properties," *Communications in Soil Science and Plant Analysis*, pp. 505-517, 2002.
- [8] A. Mekki, A. Dhouib, and S. Sayadi, "Evolution of several soil properties following amendment with olive mill wastewater," *Elsevier Progress in Natural Science*, vol. 19, pp. 1515–1521, 2009.
- [9] N. G. Nair and J. Markham, *Recycling solid waste from the olive oil extraction process / by N. G. (Tan) Nair and Julie Markham* vol. 08/165: RIRDC publication, 2008.
- [10] A. S. M. Council. (2014). *Australian Sugarcane Industry Overview*. Available: <https://asmc.com.au/industry-overview/>
- [11] S. AG, "The powerful potential of sugarcane," Siemens AG, Freyeslebenstrasse 1, 91058 Erlangen, Germany 2016.
- [12] D. o. t. E. a. Energy. (2017). *Australian Energy Update 2017*.
- [13] E. Energy, "The Outlook for Energy: A View to 2040," 2012.
- [14] D. o. E. a. Energy. (2017, 01/2018). *The Renewable Energy Target (RET) scheme*. Available: <http://www.environment.gov.au/climate-change/government/renewable-energy-target-scheme>
- [15] A. Demirbas, "Combustion characteristics of different biomass fuels," *Progress in Energy and Combustion Science*, vol. 30, pp. 219-230, 2004/01/01/ 2004.
- [16] C. Erlich, E. Björnbom, D. Bolado, M. Giner, and T. H. Fransson, "Pyrolysis and gasification of pellets from sugar cane bagasse and wood," *Fuel*, vol. 85, pp. 1535-1540, 2006/07/01/ 2006.
- [17] O. Senneca, "Kinetics of pyrolysis, combustion and gasification of three biomass fuels," *Fuel Processing Technology*, vol. 88, pp. 87-97, 2007/01/01/ 2007.
- [18] A. Roig, M. L. Cayuela, and M. A. Sánchez-Monedero, "An overview on olive mill wastes and their valorisation methods," *Elsevier Waste Management*, vol. 26, pp. 960–969, 2006.



- [19] Y.-F. Huang, P.-T. Chiueh, and S.-L. Lo, "A review on microwave pyrolysis of lignocellulosic biomass," *Sustainable Environment Research*, vol. 26, pp. 103-109, 2016/05/01/ 2016.
- [20] P. T. Williams and N. Nugranad, "Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks," *Energy*, vol. 25, pp. 493-513, 2000/06/01/ 2000.
- [21] C. Erlich, M. Öhman, E. Björnbom, and T. H. Fransson, *Thermochemical characteristics of sugar cane bagasse pellets* vol. 84, 2005.
- [22] H. B. Goyal, D. Seal, and R. C. Saxena, "Bio-fuels from thermochemical conversion of renewable resources: A review," *Renewable Sustainable Energy Rev.*, vol. 12, p. 504, 2008.
- [23] J. Yanik, C. Kornmayer, M. Saglam, and M. Yüksel, "Fast pyrolysis of agricultural wastes: Characterization of pyrolysis products," *Elsevier Fuel Processing Technology*, vol. 88, pp. 942–947, October 2007 2007.
- [24] V. Volli, R. K. Singh, and S. Murugan, "The Use of Mustard Cake Pyrolytic Oil Blends as Fuel in a Diesel Engine," *Waste and Biomass Valorization*, pp. 1-8, 2013/10/06 2013.
- [25] G. W. Huber, S. Iborra, and A. Corma, "Synthesis of transportation fuels from biomass: chemistry, catalyst and engineering.," *Chem. Rev.* 106:4044–4098, 2006.
- [26] G. W. E. Huber, "Breaking the chemical and engineering barriers to lignocellulosic biofuels: Next generation hydrocarbon biorefineries," University of Massachusetts, National Science Foundation, Chemical, Bioengineering, Environmental, and Transport Systems Division, Washington DC. June 25-26, 2008 2008.
- [27] D. Carpenter, T. L. Westover, S. Czernik, and W. Jablonski, "Biomass feedstocks for renewable fuel production: a review of the impacts of feedstock and pretreatment on the yield and product distribution of fast pyrolysis bio-oils and vapors," *Green Chemistry*, vol. 16, pp. 384-406, 2014.
- [28] Z. A. Ghani, I. N. M. Khamil, M. R. M. Isa, M. A. B. Jamaluddin, M. A. M. Ishak, and K. Ismail, "Pyrolysis of *Jatropha curcas* L. husk: Optimization solid, liquid and gas yield by using response surface methodology (RSM)," in *Sustainable Energy & Environment (ISESEE), 2011 3rd International Symposium & Exhibition in*, 2011, pp. 78-83.
- [29] E. Önal, B. B. Uzun, and A. E. Pütün, "The effect of pyrolysis atmosphere on bio-oil yields and structure," *International Journal of Green Energy*, vol. 14, pp. 1-8, 2017/01/02 2017.
- [30] W. Liang, C. Jianmeng, and F. Mengxiang, "Pyrolysis Characteristics of Lignite in a Fluidized Bed: Influence of Pyrolysis Temperature," in *Energy and Environment Technology, 2009. ICEET '09. International Conference on*, 2009, pp. 257-261.
- [31] A. V. Bridgwater, D. Meier, and D. Radlein, "An overview of fast pyrolysis of biomass," *Org. Geochem.*, vol. 30, p. 1479, 1999.
- [32] C. L. Yiin, S. Yusup, A. T. Quitain, Y. Uemura, M. Sasaki, and T. Kida, "Thermogravimetric analysis and kinetic modeling of low-transition-temperature mixtures pretreated oil palm empty fruit bunch for possible maximum yield of

- pyrolysis oil," *Bioresource Technology*, vol. 255, pp. 189-197, 2018/05/01/ 2018.
- [33] W. T. Tsai, M. K. Lee, and Y. M. Chang, "Fast pyrolysis of rice husk: Product yields and compositions," *Bioresource Technology*, vol. 98, pp. 22-28, 2007/01/01/ 2007.
- [34] OECD/IEA, " World Energy Outlook 2004)."
- [35] E. T. S. Shafiee, " When will fossil fuel reserves be diminished?," *Energy Policy*, 2009.
- [36] H. Longwell, "The Future of the Oil and Gas Industry: Past Approaches, New Challenges.," *World Energy Source*, 2002.
- [37] B. Petroleum, " BP statistical Review of World Energy. Available from: <http://www.bp.com/statisticalreview..>"
- [38] Available:  
[http://www.letu.edu/\\_Academics/Engineering/engineering/welding/research.htm](http://www.letu.edu/_Academics/Engineering/engineering/welding/research.htm)
- [39] A. B. o. Statistics. (19/02/2013). *4602.0.55.005 - Waste Account, Australia, Experimental Estimates, 2013*.
- [40] B. Dally and P. Mullinger, "Utilization of Olive Husks for Energy Generation: A Feasibility Study," University of Adelaide 2002.
- [41] R. Sterk. (2016). *U.S.D.A. sees lower world sugar stocks*. Available: [http://www.bakingbusiness.com/articles/news\\_home/Purchasing/2016/05/USDA\\_sees\\_lower\\_world\\_sugar\\_st.aspx?ID={2C1E3AC7-B2E6-4809-A34C-775012C38225}&cck=1](http://www.bakingbusiness.com/articles/news_home/Purchasing/2016/05/USDA_sees_lower_world_sugar_st.aspx?ID={2C1E3AC7-B2E6-4809-A34C-775012C38225}&cck=1)
- [42] M. M. f. I. a. B. R. VICTOR DOMINELLO. (2016). *Biofuels Regulation 2016, under the Biofuels Act 2007*. Available: [http://www.austlii.edu.au/au/legis/nsw/num\\_reg/ba2007br20162016539126a2016411.pdf](http://www.austlii.edu.au/au/legis/nsw/num_reg/ba2007br20162016539126a2016411.pdf)
- [43] X. Miao and Q. Wu, "High yield bio-oil production from fast pyrolysis by metabolic controlling of *Chlorella protothecoides*," *Journal of Biotechnology*, vol. 110, pp. 85-93, 5/13/ 2004.
- [44] F. Ren, S. A. Kanaan, M. M. Majewska, G. D. Keskar, S. Azoz, H. Wang, *et al.*, "Increase in the yield of (and selective synthesis of large-diameter) single-walled carbon nanotubes through water-assisted ethanol pyrolysis," *Journal of Catalysis*, vol. 309, pp. 419-427, 1// 2014.
- [45] S.-S. Liaw, S. Zhou, H. Wu, and M. Garcia-Perez, "Effect of pretreatment temperature on the yield and properties of bio-oils obtained from the auger pyrolysis of Douglas fir wood," *Fuel*, vol. 103, pp. 672-682, 1// 2013.
- [46] T. S. Nguyen, M. Zabeti, L. Lefferts, G. Brem, and K. Seshan, "Catalytic upgrading of biomass pyrolysis vapours using faujasite zeolite catalysts," *Biomass and Bioenergy*, vol. 48, pp. 100-110, 1// 2013.
- [47] D. A. Ruddy, J. A. Schaidle, J. R. Ferrell III, J. Wang, L. Moens, and J. E. Hensley, "Recent advances in heterogeneous catalysts for bio-oil upgrading via "ex situ catalytic fast pyrolysis": catalyst development through the study of model compounds," *Green Chemistry*, vol. 16, pp. 454-490, 2014.
- [48] M. Brebu, T. Tamminen, L. Hannevold, M. Stöcker, and I. Spiridon, "Catalytic upgrading of co-pyrolysis oils from bisphenol A polycarbonate and lignins," *Polymer Degradation and Stability*, vol. 102, pp. 88-94, 4// 2014.

- [49] İ. Demiral and Ş. Ç. Kul, "Pyrolysis of apricot kernel shell in a fixed-bed reactor: Characterization of bio-oil and char," *Journal of Analytical and Applied Pyrolysis*, 2014.
- [50] C. Analytical. *Analysis of Sugarcane Bagasse*.
- [51] G. F. Hutasoit and A. Toharisman, "Composting of sugarcane bagasse," *Berita - Pusat Penelitian Perkebunan Gula Indonesia*, pp. 85-87, 1994.
- [52] A. Sales and S. A. Lima, "Use of Brazilian sugarcane bagasse ash in concrete as sand replacement," *Waste Management*, vol. 30, pp. 1114-1122, 2010/06/01/ 2010.
- [53] S. R. Teixeira, A. E. De Souza, G. T. De Almeida Santos, A. F. Vilche Peña, and Á. G. Miguel, "Sugarcane Bagasse Ash as a Potential Quartz Replacement in Red Ceramic," *Journal of the American Ceramic Society*, vol. 91, pp. 1883-1887, 2008.
- [54] C. F. Assist, "Brazil Low Carbon Country Case Study," ESMAP, [http://sdwebx.worldbank.org/climateportalb/doc/ESMAP/FINAL\\_LCCGP\\_Brazil.pdf2010](http://sdwebx.worldbank.org/climateportalb/doc/ESMAP/FINAL_LCCGP_Brazil.pdf2010).
- [55] K. Hofsetz and M. A. Silva, "Brazilian sugarcane bagasse: Energy and non-energy consumption," *Biomass and Bioenergy*, vol. 46, pp. 564-573, 2012/11/01/ 2012.
- [56] R. Brown and C. C. Stevens, *Thermochemical Processing of Biomass : Conversion into Fuels, Chemicals and Power*. Hoboken, NJ, USA Wiley, 2011.
- [57] B. Jeffrey, D. Nettleton, N. Kuzhiyil, M. Rover, R. Brown, K. Lamkey, *et al.*, "Significant Variation for Bio-oil Compounds After Pyrolysis/Gas Chromatography–Mass Spectrometry of Cobs and Stover Among Five Near-Isogenic Brown Midrib Hybrids in Maize," *BioEnergy Research*, vol. 7, pp. 693-701, 2014/06/01 2014.
- [58] H. Yang, R. Yan, H. Chen, D. H. Lee, D. T. Liang, and C. Zheng, "Pyrolysis of palm oil wastes for enhanced production of hydrogen rich gases," *Fuel Processing Technology*, vol. 87, pp. 935-942, 10// 2006.
- [59] M. Jahirul, M. Rasul, A. Chowdhury, and N. Ashwath, "Biofuels Production through Biomass Pyrolysis —A Technological Review," *Energies*, vol. 5, pp. 4952-5001, 2012.
- [60] J. M. Andrésen, J. J. Strohm, L. Sun, and C. Song, "Relationship between the Formation of Aromatic Compounds and Solid Deposition during Thermal Degradation of Jet Fuels in the Pyrolytic Regime," *Energy & Fuels*, vol. 15, pp. 714-723, 2001/05/01 2001.
- [61] M. Lapuerta, O. Armas, and J. Rodríguez-Fernández, "Effect of biodiesel fuels on diesel engine emissions," *Progress in Energy and Combustion Science*, vol. 34, pp. 198-223, 2008/04/01/ 2008.
- [62] C. D. Rakopoulos, K. A. Antonopoulos, D. C. Rakopoulos, D. T. Hountalas, and E. G. Giakoumis, "Comparative performance and emissions study of a direct injection Diesel engine using blends of Diesel fuel with vegetable oils or biodiesels of various origins," *Energy Conversion and Management*, vol. 47, pp. 3272-3287, 2006/11/01/ 2006.
- [63] C. A. Mullen, G. D. Strahan, and A. A. Boateng, "Pyrolysis Oil—Overview of Characterization and Utilization," *Energy & Fuels*, vol. 23, 2009.
- [64] Y. Li and S. K. Khanal, *Bioenergy: Principles and Applications*: Wiley, 2016.

- [65] C. Williams. *Bioenergy Conversion Technologies*. Available: <http://www.wgbn.wisc.edu/conversion/bioenergy-conversion-technologies#Thermal%20conversion>
- [66] A. Demirbas, "Progress and recent trends in biofuels," *Progress in Energy and Combustion Science*, vol. 33, pp. 1-18, 2007 2007.
- [67] F. Miller and F. Metting Jr, "Composting as a process based on the control of ecologically selective factors," *Soil microbial ecology: applications in agricultural and environmental management.*, pp. 515-544, 1992.
- [68] P. A. M. Claassen, J. B. van Lier, A. M. Lopez Contreras, E. W. J. van Niel, L. Sijtsma, A. J. M. Stams, *et al.*, "Utilisation of biomass for the supply of energy carriers," *Applied Microbiology and Biotechnology*, vol. 52, pp. 741-755, 1999/11/01 1999.
- [69] J. Mata-Alvarez, S. Macé, and P. Llabrés, "Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives," *Bioresource Technology*, vol. 74, pp. 3-16, 8// 2000.
- [70] Y. Chen, J. J. Cheng, and K. S. Creamer, "Inhibition of anaerobic digestion process: A review," *Bioresource Technology*, vol. 99, pp. 4044-4064, 7// 2008.
- [71] H. Wagner and M. Kaltschmitt, "Biochemical and thermochemical conversion of wood to ethanol—simulation and analysis of different processes," *Biomass Conversion and Biorefinery*, vol. 3, pp. 87-102, 2013/06/01 2013.
- [72] M. Balat, M. Balat, E. Kırtay, and H. Balat, "Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 2: Gasification systems," *Sila Science and Energy Company, University Mah, Trabzon, Turkey Energy Conversion and Management* 2009.
- [73] D. Mohan, J. Charles U. Pittman, and P. H. Steele, "Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review," *ACS Energy and Fuels, American Chemical Society*, pp. 848–889, March 10 2006.
- [74] G. Taralas and M. G. Kontominas, "Pyrolysis of solid residues commencing from the olive oil food industry for potential hydrogen production," *Journal of Analytical and Applied Pyrolysis*, vol. 76, pp. 109-116, 6// 2006.
- [75] J. Charles U. Pittman, D. Mohan, A. Eseyin, Q. Li, L. Ingram, E.-B. M. Hassan, *et al.*, "Characterization of Bio-oils Produced from Fast Pyrolysis of Corn Stalks in an Auger Reactor," *ACS Energy and Fuels, American Chemical Society*, pp. 3816–3825, April 16 2012.
- [76] İ. Demiralpa, A. Eryazıcıb, and S. Şensöz, "Bio-oil production from pyrolysis of corncob (*Zea mays L.*)," *Elsevier Biomass and Bioenergy*, vol. 36, pp. 43–49, January 2012.
- [77] C. U. Pittman, D. Mohan, A. Eseyin, Q. Li, L. Ingram, E.-B. M. Hassan, *et al.*, "Characterization of Bio-oils Produced from Fast Pyrolysis of Corn Stalks in an Auger Reactor," *ACS Energy and Fuels, American Chemical Society*, vol. 26, p. 3816 – 3825, 2012.
- [78] G. Jie, L. Ying-Shun, and L. Mai-Xi, "Product characterization of waste printed circuit board by pyrolysis," *Journal of Analytical and Applied Pyrolysis*, vol. 83, pp. 185-189, 11// 2008.
- [79] S. A. Groves, R. S. Lehrle, M. Blazsó, and T. Székely, "Natural rubber pyrolysis: Study of temperature-and thickness-dependence indicates dimer

- formation mechanism," *Journal of Analytical and Applied Pyrolysis*, vol. 19, pp. 301-309, 7// 1991.
- [80] C. Roy, H. Darmstadt, B. Benallal, and C. Amen-Chen, "Characterization of naphtha and carbon black obtained by vacuum pyrolysis of polyisoprene rubber," *Fuel Processing Technology*, vol. 50, pp. 87-103, 1// 1997.
- [81] A. V. Bridgwater, "Principles and practice of biomass fast pyrolysis processes for liquids," *Journal of Analytical and Applied Pyrolysis*, vol. 51, pp. 3-22, 7// 1999.
- [82] C. S. Robert Brown, *Thermochemical Processing of Biomass : Conversion into Fuels, Chemicals and Power*. New York: Wiley, 2011.
- [83] T. Bridgwater, "Pyrolysis of Biomass," *IEA Bioenergy: Task 34; Bioenergy Research Group, Aston University: Birmingham, UK*, 2007.
- [84] G. Maschio, C. Koufopoulos, and A. Lucchesi, "Pyrolysis, a promising route for biomass utilization," *Bioresource Technology*, vol. 42, pp. 219-231, 1992 1992.
- [85] J. Yodera, S. Galinatob, D. Granatsteinc, and M. Garcia-Pérezd, "Economic tradeoff between biochar and bio-oil production via pyrolysis," *Elsevier Biomass and Bioenergy*, vol. 35, pp. 1851–1862, 2011.
- [86] A. R. S. B. I. U.S. Department of Agriculture. (2009).
- [87] R. Ibarrola, S. Shackley, and J. Hammond, "Pyrolysis biochar systems for recovering biodegradable materials: A life cycle carbon assessment," *Waste Management*, vol. 32, pp. 859-868, 2012/05/01/ 2012.
- [88] A. E. S. Green, "Process and device for pyrolysis of feedstock," ed: Google Patents, 2004.
- [89] C. H. Lim, I. Y. Mohammed, Y. A. Abakr, F. K. Kazi, S. Yusup, and H. L. Lam, "Novel input-output prediction approach for biomass pyrolysis," *Journal of Cleaner Production*, vol. 136, pp. 51-61, 2016/11/10/ 2016.
- [90] A. A. C. a. M. G. R. Mohammed J. Kabir, "Pyrolysis of Municipal Green Waste: A Modelling, Simulation and Experimental Analysis," *Energies 2015*, pp. 7522-7541, 2015.
- [91] V. Benavente, E. Calabuig, and A. Fullana, "Upgrading of moist agro-industrial wastes by hydrothermal carbonization," *Journal of Analytical and Applied Pyrolysis*, vol. 113, pp. 89-98, 2015/05/01/ 2015.
- [92] A. M. Zmiewski, N. L. Hammer, R. A. Garrido, T. G. Misera, C. G. Coe, and J. A. Satrio, "Exploring the Products from Pinewood Pyrolysis in Three Different Reactor Systems," *Energy & Fuels*, vol. 29, pp. 5857-5864, 2015/09/17 2015.
- [93] H. Zhang, R. Xiao, H. Huang, and G. Xiao, "Comparison of non-catalytic and catalytic fast pyrolysis of corncob in a fluidized bed reactor," *Bioresource Technology*, vol. 100, pp. 1428-1434, 2009/02/01/ 2009.
- [94] J. P. Diebold, "A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-Oils," N. R. E. L. (NREL), Ed., ed. Colorado: U.S. Department of Energy, 2000, pp. 1-59.
- [95] P. Basu, *Biomass gasification, pyrolysis and torrefaction: practical design and theory*: Academic press, 2013.
- [96] P. A. Horne and P. T. Williams, "Influence of temperature on the products from the flash pyrolysis of biomass," *Fuel*, vol. 75, pp. 1051-1059, 7// 1996.

- [97] M. Garcia-Pérez, A. Chaala, and C. Roy, "Vacuum pyrolysis of sugarcane bagasse," *Journal of Analytical and Applied Pyrolysis*, vol. 65, pp. 111-136, 2002/12/01/ 2002.
- [98] S. Czernik and A. V. Bridgwater, "Overview of Applications of Biomass Fast Pyrolysis Oil," *Energy & Fuels*, vol. 18, pp. 590-598, 2004/03/01 2004.
- [99] X. Wang, S. R. A. Kersten, W. Prins, and W. P. M. van Swaaij, "Biomass Pyrolysis in a Fluidized Bed Reactor. Part 2: Experimental Validation of Model Results," *Industrial & Engineering Chemistry Research*, vol. 44, pp. 8786-8795, 2005/11/01 2005.
- [100] N. Tippayawong, J. Kinorn, and S. Thavornun, "Yields and Gaseous Composition from Slow Pyrolysis of Refuse-derived Fuels," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 30, pp. 1572-1580, 2008/07/29 2008.
- [101] J. G. Rogers and J. G. Brammer, "Estimation of the production cost of fast pyrolysis bio-oil," *Elsevier Biomass and Bioenergy*, vol. 36, pp. 208–217, January 2012.
- [102] A. V. Bridgwater and G. V. C. Peacocke, "Fast pyrolysis processes for biomass," *Renewable and Sustainable Energy Reviews*, vol. 4, pp. 1-73, 3// 2000.
- [103] H. S. Heoa, H. J. Parka, J.-H. Yimb, J. M. Sohnc, J. Parkd, S.-S. Kime, *et al.*, "Influence of operation variables on fast pyrolysis of *Miscanthus sinensis* var. *purpurascens*," *Elsevier Bioresource Technology*, vol. 101, pp. 3672–3677, May 2010.
- [104] J. D. Adjaye and N. N. Bakhshi, "Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part I: Conversion over various catalysts," *Fuel Processing Technology*, vol. 45, pp. 161-183, 12// 1995.
- [105] J. D. Adjaye and N. N. Bakhshi, "Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part II: Comparative catalyst performance and reaction pathways," *Fuel Processing Technology*, vol. 45, pp. 185-202, 12// 1995.
- [106] R. C. Brown and J. Holmgren, "Fast Pyrolysis and Bio-Oil Upgrading," ed. Miami, Florida, US: Ascension Publishing, 2009.
- [107] T. N. A. University. (01/2014). *RENEWABLE ENERGY:: (AENG 352) Principles of Pyrolysis* Available: <http://www.tnau.ac.in/eagri/eagri50/AENG352/lec10.pdf>
- [108] S. Zhang, Y. Yan, T. Li, and Z. Ren, "Upgrading of liquid fuel from the pyrolysis of biomass," *Bioresource Technology*, vol. 96, pp. 545-550, 2005 2005.
- [109] S. Sadaka and A. A. Boateng. (20/03/2014). *Pyrolysis and Bio-Oil*. Available: <http://www.uaex.edu/publications/pdf/FSA-1052.pdf>
- [110] U. S. D. o. Energy. (2014). *Fixed Bed Reactor*. Available: <http://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/fixed-bed-reactor>
- [111] U. n.-f. a. a. o. N. R. M. a. E. Department). (1994, 12). *The research progress of biomass pyrolysis processes*. Available: <http://www.fao.org/docrep/t4470e/t4470e0a.htm>



- [112] M. Usui, K. Okazaki, and K. Akamatsu, "Waste Treatment Using Induction Heating and Pyrolysis," *Fuji Electronic Journal*, vol. 73, pp. 69-73, 2000.
- [113] I. H. Solutions, "The Induction Heating Guide," *GH Induction Atmospheres*, 2013.
- [114] S. S. Lam, A. D. Russell, and H. A. Chase, "FROM WASTE TO VALUABLE FUEL: HOW MICROWAVE-HEATED PYROLYSIS CAN RECYCLE WASTE AUTOMOTIVE ENGINE OIL," *Proceedings of the American Chemical Society*, vol. 56, 2011.
- [115] U. o. Melbourne. (2013). *Microwave Assisted Pyrolysis of biosolids* Available: <http://www.smartwater.com.au/knowledge-hub/resource-recovery/biosolids-management/microwave-assisted-pyrolysis-of-biosolids.html#project-info>
- [116] R. Y. Nuwayhid, D. M. Rowe, and G. Min, "Low cost stove-top thermoelectric generator for regions with unreliable electricity supply," *Renewable Energy*, vol. 28, pp. 205-222, 2003/02/01/ 2003.
- [117] P. H. Wilks and M. L. Thorpe, "The heating of solids in high temperature plasma " 1971.
- [118] K. Zeng, D. Gauthier, J. Lu, and G. Flamant, "Parametric study and process optimization for solar pyrolysis of beech wood," *Energy Conversion and Management*, vol. 106, pp. 987-998, 2015/12/01/ 2015.
- [119] M. Sánchez, B. Clifford, and J. D. Nixon, "Modelling and evaluating a solar pyrolysis system," *Renewable Energy*, vol. 116, pp. 630-638, 2018/02/01/ 2018.
- [120] H. Yang, R. Yan, T. Chin, D. T. Liang, H. Chen, and C. Zheng, "Thermogravimetric Analysis–Fourier Transform Infrared Analysis of Palm Oil Waste Pyrolysis," *Energy & Fuels*, vol. 18, pp. 1814-1821, 2004/11/01 2004.
- [121] P. Wiczorek. *Polymer Ionics Research Group*. Available: <http://pirg.ch.pw.edu.pl/instrukcje/dsc-instr.pdf>
- [122] Available: [http://www.evitherm.org/Files/982/TherAna\\_Depository\\_MeasurementMethods\\_DiffPowerScanCalorimeter.jpg](http://www.evitherm.org/Files/982/TherAna_Depository_MeasurementMethods_DiffPowerScanCalorimeter.jpg)
- [123] hilldodger. *Training and diet talk...* Available: <http://singletrackworld.com/forum/topic/training-and-diet-talk/page/12>
- [124] L. Stockman, D. Turnbull, and S. Kretzmann, "Petroleum Coke: the coal hiding in the Tar Sands," Oilchange International, Washington DC, USA 2013.
- [125] P. G. Ball. (1998). *New pH Test Offers Benefits over TAN/TBN*. Available: <http://www.machinerylubrication.com/Read/100/ph-test-tan-tbn>
- [126] D. Özçimen and F. Karaosmanoğlu, "Production and characterization of bio-oil and biochar from rapeseed cake," *Renewable Energy*, vol. 29, pp. 779-787, 2004/04/01/ 2004.
- [127] J. Wright, "Benefits of FTIR Oil Analysis," in *Machinery*, ed. <http://www.machinerylubrication.com/Read/30205/ftir-oil-analysis>: Noria Corporation 2015.
- [128] J. Kopka, "Gas Chromatography Mass Spectrometry," in *Plant Metabolomics*, K. Saito, R. A. Dixon, and L. Willmitzer, Eds., ed Berlin, Heidelberg: Springer Berlin Heidelberg, 2006.
- [129] T. Taylor and J. Langley. *The CHROMacademy Essential Guide to Understanding Electron Ionization for GC-MS* Available:

- [130] M. R. Rover, "Analysis of sugars and phenolic compounds in biooil," Doctor of Philosophy, Mechanical Engineering, Iowa State University, Iowa, 2013.
- [131] A. E. Pütün, A. Özcan, and E. Pütün, "Pyrolysis of hazelnut shells in a fixed-bed tubular reactor: yields and structural analysis of bio-oil," *Journal of Analytical and Applied Pyrolysis*, vol. 52, pp. 33-49, 9// 1999.
- [132] W. T. Tsai, M. K. Lee, and Y. M. Chang, "Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor," *Journal of Analytical and Applied Pyrolysis*, vol. 76, pp. 230-237, 6// 2006.
- [133] Ö. Onay, S. H. Beis, and Ö. M. Koçkar, "Fast pyrolysis of rape seed in a well-swept fixed-bed reactor," *Journal of Analytical and Applied Pyrolysis*, vol. 58-59, pp. 995-1007, 4/1/ 2001.
- [134] Y. Shinogi and Y. Kanri, "Pyrolysis of plant, animal and human waste: physical and chemical characterization of the pyrolytic products," *Bioresource Technology*, vol. 90, pp. 241-247, 12// 2003.
- [135] C. Acikgoz, O. Onay, and O. M. Kockar, "Fast pyrolysis of linseed: product yields and compositions," *Journal of Analytical and Applied Pyrolysis*, vol. 71, pp. 417-429, 6// 2004.
- [136] M. F. Laresgoiti, B. M. Caballero, I. de Marco, A. Torres, M. A. Cabrero, and M. J. Chomón, "Characterization of the liquid products obtained in tyre pyrolysis," *Journal of Analytical and Applied Pyrolysis*, vol. 71, pp. 917-934, 6// 2004.
- [137] F. Ateş, E. Pütün, and A. E. Pütün, "Fast pyrolysis of sesame stalk: yields and structural analysis of bio-oil," *Journal of Analytical and Applied Pyrolysis*, vol. 71, pp. 779-790, 6// 2004.
- [138] S. C. Rabelo, H. Carrere, R. Maciel Filho, and A. C. Costa, "Production of bioethanol, methane and heat from sugarcane bagasse in a biorefinery concept," *Bioresource Technology*, vol. 102, pp. 7887-7895, 2011/09/01/ 2011.
- [139] T. Tana, Z. Zhang, L. Moghaddam, D. W. Rackemann, J. Rencoret, A. Gutiérrez, *et al.*, "Structural Changes of Sugar Cane Bagasse Lignin during Cellulosic Ethanol Production Process," *ACS Sustainable Chemistry & Engineering*, vol. 4, pp. 5483-5494, 2016.
- [140] M. E. da Cunha, J. K. Schneider, M. C. Brasil, C. A. Cardoso, L. R. Monteiro, F. L. Mendes, *et al.*, "Analysis of fractions and bio-oil of sugar cane straw by one-dimensional and two-dimensional gas chromatography with quadrupole mass spectrometry (GC×GC/qMS)," *Microchemical Journal*, vol. 110, pp. 113-119, 2013/09/01/ 2013.
- [141] B. B. Popov, S. Najman, V. K. Hristova, and M. A. Ahmad, "Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) Approach for the Determination of Heavy Metals, Metalloid and Trace Element in Soil and Vegetables," *Indian Horticulture Journal (IHJ)*, ISSN, pp. 2249-6823, 2014.
- [142] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, *et al.*, "Determination of structural carbohydrates and lignin in biomass," *Laboratory analytical procedure*, vol. 1617, pp. 1-16, 2008.
- [143] C. Sheng and J. Azevedo, "Estimating the higher heating value of biomass fuels from basic analysis data," *Biomass and Bioenergy*, vol. 28, pp. 499-507, 2005.


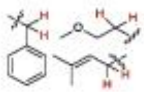
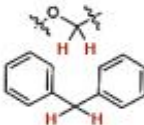
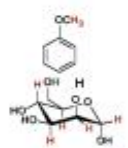
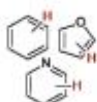



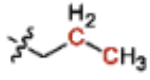
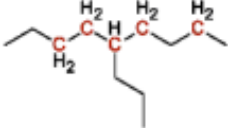
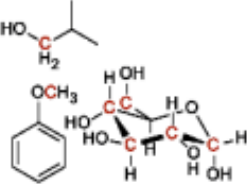
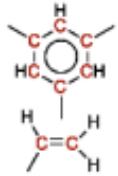


- [144] W. Pippo, C. Luengo, L. Alberteris, G. Garcia del Pino, and J. Neto, *Energy Recovery from Sugarcane: Study of Heating Value Variations of Sugarcane-trash with Moisture Content during the Milling Season*, 2014.
- [145] K. Crombie, O. Mašek, S. P. Sohi, P. Brownsort, and A. Cross, "The effect of pyrolysis conditions on biochar stability as determined by three methods," *Gcb Bioenergy*, vol. 5, pp. 122-131, 2013.
- [146] A. Enders, K. Hanley, T. Whitman, S. Joseph, and J. Lehmann, "Characterization of biochars to evaluate recalcitrance and agronomic performance," *Bioresource technology*, vol. 114, pp. 644-653, 2012.
- [147] R. French and S. Czernik, "Catalytic pyrolysis of biomass for biofuels production," *Fuel Processing Technology*, vol. 91, pp. 25-32, 2010/01/01/ 2010.
- [148] A. R. Ardiyanti, S. A. Khromova, R. H. Venderbosch, V. A. Yakovlev, and H. J. Heeres, "Catalytic hydrotreatment of fast-pyrolysis oil using non-sulfided bimetallic Ni-Cu catalysts on a  $\delta$ -Al<sub>2</sub>O<sub>3</sub> support," *Applied Catalysis B: Environmental*, vol. 117-118, pp. 105-117, 2012/05/18/ 2012.

## 8 Appendices

### 8.1 Oil Composition Based on Feedstock

Table 15: Percentage of hydrogen of bio oil derived from the pyrolysis process [63]

Chemical Shifts (ppm)	Proton Assignment	switch-grass	alfalfa stems	corn stover	guayule -whole	guayule bagasse	chicken litter
0.5–1.5	 <p>Alkanes</p>	9.8%	20.9%	11.8%	29.4%	28.7%	34.6%
1.5–3.0	 <p>aliphatics <math>\alpha</math>-to heteroatom or unsaturation</p>	24.3%	54.0%	18.3%	42.0%	34.5%	45.9%
3.0–4.4	 <p>alcohols, methylene-dibenzene</p>	21.3%	7.2%	20.5%	10.4%	12.5%	9.8%
4.4–6.0	 <p>methoxy, carbohydrates</p>	25.7%	2.3%	30.3%	6.8%	9.7%	1.8%
6.0 - 8.5	 <p>(hetero-) aromatics</p>	17.5%	15.1%	15.1%	11.2%	15.6%	7.9%
9.5 - 10.1	 <p>aldehydes</p>	1.3%	-	1.7%	0.2%	0.5%	-

Chemical Shifts (ppm)	Carbon assignments*	switch-grass	alfalfa stems	corn stover	guayule – whole	guayule bagasse	chicken litter
0–28	 short aliphatics	13.8%	17.2%	13.8%	28.5%	19.1%	25.8%
28–55	 long and branched aliphatics	7.3%	12.2%	10.3%	24.4%	29.0%	21.8%
0-55 Total	All of above	21.1%	29.4%	24.1%	52.9%	48.1%	47.6%
55–95	 alcohols, ethers, phenolic-methoxys, carbohydrates sugars	24.7%	16.1%	30.8%	6.7%	7.7%	13.6%
95-165	 aromatics, olefins	53.0%	51.9%	36.0%	39.5%	43.5%	36.2%
165-180	 esters, carboxylic acids	-	2.6%	3.8%	0.8%	0.4%	-
180-215	 ketones, aldehydes	1.2%	-	1.5%	0.1%	0.2%	2.6%

\* ) The strong acetone solvent resonances at 30 ppm (CH<sub>3</sub>) and 207 ppm (C=O) were excluded from this analysis. Source: Mullen, C.A., Strahan, G.D., and Boateng, A.A. Energy & Fuels 23:2707-2718. 2009.

## 8.2 Bio Oil Composition Limits

Table 16: Bio oil composition

Compound	Wood Distillate	Smoke Flavors	Bio-Oils wt%
<b>Acids</b>			
Formic (methanoic)	f,g,h,k,s,v	GI,m,t	0.3-9.1
Acetic (ethanoic)	f,g,h,k,s,v	GI,m,t	0.5-12
Propanoic	f,g,h,k,s,v	GI,m	0.1-1.8
Hydroxyacetic	f, , ,s,v	M	0.1-0.9
2-Butenic(erotonic)	f,g,h,k,s,v	M	---
Butanoic	f,g,h,k,s,v	T	0.1-0.5
Pentanoic (valeric)	f, ,h,k,s,v	GI,m,t	0.1-0.8
2-Me butanoic	f, ,h,k,s	M	---
4-Oxypentanoic	, , ,s,v	GI,m	0.1-0.4
4-Hydroxypentanoic	, , , , ,v		---
Hexanoic (caproic)	f, ,h, ,s	M	0.1-0.3
Benzoic		m,t	0.2-0.3
Heptanoic	---	M	0.3
<b>Esters</b>			
Methyl formate	f, ,h, ,s	m,t	0.1-0.9
Methyl acetate	f, ,h,k,s,v	m,t	---
Methyl propionate	f, ,h, , ,v	M	---
Butyrolactone	g, , ,s,v	m,t	0.1-0.9
Methyl Crotonate	---	M	---
Methyl n-butyrate	f, ,h, , ,	m,t	---
Valerolactone	f, ,h,k,s,v	---	0.2
Angelicalactone	---	M	0.1-1.2
Methyl valerate	f, ,h, ,	GI,m,t	---
<b>Aldehydes</b>			
Formaldehyde	, , ,h, , ,	m,t	0.1-3.3
Acetaldehyde	f,g,h,k,s,v	GI,m,t	0.1-8.5
2-Propenal (acrolein)	---	m	0.6-0.9
2-Butenal	, , , , , ,v	m	trace
2-Methyl-2-butenal	---	GI,m	0.1-0.5
Pentanal	f, ,h, , ,v	m	0.5
Ethanedial	---	---	0.9-4.6
<b>Alcohols</b>			
Methanol	f,g,h,k,s,v	m,t	0.4-2.4
Ethanol	g, , , ,v	m,t	0.6-1.4
2-Propanol-1-ol	f, ,h,k,s	m,t	---
Isobutanol	f, ,h,k, ,v	m	---
3-Methyl-1-butanol	, , , , ,s	---	---
Ethylene glycol	---	m	0.7-2.0
<b>Ketones</b>			
Acetone	f, ,h,k,s,v	m,t	2.8
2-Butanone (MEK)	f,g,h,k,s,v	d	---
2,3-Butandione	, , , , ,v	m	0.3-0.9
Cyclo pentanone	f, ,h, ,s,v	m,t	---
2-Pentanone	f, , , , ,v	m	---
3-Pentanone	, ,h, , , ,	m	---
2-Cyclopentanone	, , , , ,v	GI,m	---
2,3-Pentenedione	, , , , ,v	m,t	0.2-0.4
3Me2cyclopenten-2-ol-one	f, , , , , ,v	m	0.1-0.6
Me-cyclopentanone	f, ,h, ,s,v	m	---
2-Hexanone	---	m	---
Cyclo hexanone	---	m	trace
Methylcyclohexanone	f, , , ,	---	---
2-Et-cyclopentanone	---	t	0.2-0.3
Dimethylcyclopentanone	---	m	0.3
Trimethylcyclopentanone	---	GI	0.1-0.5
Trimethylcyclopentanone	---	m	0.2-0.4
<b>Phenols</b>			
Phenol	f, ,h, ,s,v	GI,m,t	0.1-3.8
2-Methyl phenol	f, ,h, ,s,v	GI,m,t	0.1-0.6
3-Methyl phenol	f, ,h, ,s,v	GI,m,t	0.1-0.4
4-Methyl phenol	f, ,h, , ,v	GI,m,t	0.1-0.5
2,3 Dimethyl phenol	, , , , ,s,v	GI,m,t	0.1-0.5
2,4 Dimethyl phenol	f, ,h, ,s,v	GI,m,t	0.1-0.3
2,5 Dimethyl phenol	, , , , ,s,v	GI,m,t	0.2-0.4
2,6 Dimethyl phenol	, , , , ,s,v	GI,m,t	0.1-0.4
3,5 Dimethyl phenol	f, ,h, ,s,v	m,t	---
2-Ethylphenol	f, , , , , ,	GI,m,t	0.1-1.3
2,4,6 TriMe phenol	---	m	0.3
1,2 DiOH benzene	f, ,h,k,s,v	GI,m,t	0.1-0.7
1,3 DiOH benzene	---	m	0.1-0.3
1,4 DiOH benzene	---	---	0.1-1.9
4-Methoxy catechol	---	GI,m,t	0.6
1,2,3 Tri-OH-benzene	, ,h, ,s	t	0.6

d---Doerr et al. (1966)  
G---Guillén et al. (1995)  
GI---Guillén and Ibarra (1996)  
m---Maga (1987 and 1988)  
t---Toth and Posthast (1984)

f---Friaps (1901)  
g---Goos and Reiter (1946)  
h---Hawley (1923)  
k---Klar (1925)  
s---Stamm and Harris (1953)  
v---Vergnet and Villeneuve (1988)

Compound	Wood Distillate	Smoke Flavors	Bio-Oils wt%
----------	-----------------	---------------	--------------

**Alkenes**

2-Methyl propene	---	---	---
Dimethylcyclopentene	---	---	0.7
Alpha-pinene	, , , , , s,	---	---
Dipentene	, , , , , s,	---	---

**Aromatics**

Benzene	, , , k, , , v	m	---
Toluene	f, , h, k, s, v	G, m	---
Xylenes	f, , h, k, s	---	---
Naphthalene	, , , , , s, v	t	---
Phenanthrene	---	t	---
Fluoranthene	---	t	---
Chrysene	, , , k, , ,	t	---

**Nitrogen Compounds**

Ammonia	, , h, k, s,	---	---
Methyl amine	f, , h, k, s,	m	---
Pyridine	, , h, , s,	m	---
Methyl pyridine	, , h, , s,	---	---

Compound	Wood Distillate	Smoke Flavors	Bio-Oils wt%
----------	-----------------	---------------	--------------

**Furans**

Furan	, , , , , v	M, t	0.1-0.3
2-Methyl furan	f, , h, , , ,	m, t	0.1-0.2
2-Furanone	Gf	Gf	0.1-1.1
Furfural	f, , h, k, s, v	G, Gf, m, t	0.1-1.1
3-Methyl-2(3H)furanone	---	G, Gf	0.1
Furfural alcohol	, , , , , s, v	Gf, m, t	0.1-5.2
Furoic acid	, , h, k, s,	m	0.4
Methyl furoate	, g, , , , v	m, t	---
5-Methylfurfural	f, , h, k, s, v	G, m, t	0.1-0.6
5-OH-methyl-2-furfural	, , , , , s,	m	0.3-2.2
Dimethyl furan	f, , h, , , ,	m	---

**Misc. Oxygenates**

Hydroxyacetaldehyde	---	m, t	0.9-1.3
Acetyl (hydroxyacetone)	, , , , , s, v	m, t	0.7-7.4
Methylal	f, , k, s,	m	---
Dimethyl acetal	, , h, k, s,	m	---
Acetal	---	---	0.1-0.2
Acetyloxy-2-propanone	---	m	0.8
2-OH-3-Me-2-cyclopentene-1-one	---	m	0.1-0.5
Methyl cyclopentenolone	---	m	0.1-1.9
1-Acetyloxy-2-propanone	---	G, Gf	0.1
2-Methyl-3-hydroxy-2-pyrone	---	---	0.2-0.4
2-Methoxy-4-methylanisole	---	---	0.1-0.4
4-OH-3-methoxybenzaldehyde	---	G, Gf, m	0.1-1.1
Maltol	, g, , , s,	G, Gf, m, t	---

Compound	Wood Distillate	Smoke Flavors	Bio-Oils wt%
----------	-----------------	---------------	--------------

**Guaiaacols**

2-Methoxy phenol	f, g, h, , s, v	G, Gf, m, t	0.1-1.1
4-Methyl guaiacol	, , , , , v	G, Gf, m, t	0.1-1.9
Ethyl guaiacol	f, g, h, , , v	G, Gf, m, t	0.1-0.6
Eugenol	, , , , , v	Gf, m, t	0.1-2.3
Isoeugenol	, , , , , v	Gf, m, t	0.1-7.2
4-Propylguaiacol	f, , h, , , v	G, Gf, m, t	0.1-0.4
Acetoguaiacone	---	---	0.8
Propioguaiacone	---	---	0.8

**Syringols**

2,6-DiOMe phenol	f, g, h, , , v	G, Gf, m, t	0.7-4.8
Methyl syringol	f, , h, , , v	G, Gf, m, t	0.1-0.3
4-Ethyl syringol	, , , , , v	G, Gf, m, t	0.2
Propyl syringol	f, , h, , , v	G, Gf, m, t	0.1-1.5
Syringaldehyde	, , , , , v	G, Gf, m, t	0.1-1.5
4-Propenylsyringol	, , , , , v	G, Gf, m, t	0.1-0.3
4-OH-3,5-diOMe phenyl ethanone	G, Gf	G, Gf	0.1-0.3

**Sugars**

Levoglucofan	, , , , s,	---	0.4-1.4
Glucose	---	---	0.4-1.3
Fructose	---	---	0.7-2.9
D-xylose	---	---	0.1-1.4
D-Arabinose	---	---	0.1
Cellobiosan	---	---	0.6-3.2
1,6 Anhydroglucofuranose	---	---	3.1

f---Fraps (1901)  
g---Goos and Reiter (1946)  
h---Hawley (1923)  
k---Klar (1925)  
s---Stamm and Harris (1953)  
v---Vergnet and Villeneuve (1988)

G---Guillén et al. (1995)  
Gf---Guillén and Ibarogitia (1996)  
m---Maga (1987 and 1988)  
t---Tóth and Pothast (1984)

### 8.3 Analysis legends and tables

FTIR functional groups in bio-crude produced at full temperature range

Frequency (cm <sup>-1</sup> )	Group	Class of component
3335	O-H stretching	Polymeric O-H, phenolic O-H, water
2966, 2937, 2849	C-H stretching	Alkanes
1708	C=O stretching	Ketones, carboxylic acids, aldehydes, esters, acyls
1605, 1594	C=C stretching	Alkenes
1512, 1501	Aromatic C=C stretching	Aromatic compounds, furfuryl groups
1454, 1378, 1362	C-H bending	Alkanes
1215	C-O-C	Ethers, alcohols
1123	CH <sub>2</sub> -O-CH <sub>2</sub>	Sugars, levoglucosan
1037		glycosidic unit
993	CH <sub>2</sub> out-of-plane twist	
833	C-H in-plane bending	Aromatic compounds
753	C-H out-of-plane deformation vibrations	

FTIR functional groups in bio-crude produced at scaled down temperature range

Frequency (cm <sup>-1</sup> )	Group	Class of component
3335	O-H stretching	Polymeric O-H, phenolic O-H, water
2966, 2937, 2849	C-H stretching	Alkanes
1693	C=O stretching	Ketones, carboxylic acids, aldehydes, esters, acyls
1558	C=C stretching	Alkenes
1435	C-H bending	Alkanes
1232	C-O	Ethers, alcohols
1159	C-O-C	Ethers, alcohols
1096	C-O stretch	may be graphite
1037		glycosidic unit
862	C-H in-plane bending	Aromatic compounds
791		
746	C-H out-of-plane deformation vibrations	

Calorific analysis of bio-crude oil produced at full temperature range

Sample	Nitrogen	Carbon	Hydrogen	Sulphur	Oxygen	HHV (MJ/kg)
<b>Solid Particles</b>						
300C	0	15.62	9.28	0	59.19	9.7
300C	0	14.88	8.54	0	58.25	8.68
400C	0	18.97	8.85	0	52.28	11.15
400C	0	19.18	9.26	0	54.69	11.43
500C	0	19.29	9.59	0	53.86	11.95
500C	0	19.33	9.6	0	57.1	11.61
600C	0	19.09	9.03	0	68.12	9.64
600C	0	19.27	9.28	0	70.8	9.69
<b>Oil Output</b>						
300C	0	65.56	3.41	0	11.45	25.74
300C	0	66.01	3.49	0	10.66	26.08
400C	0.51	56.1	3.04	0	9.39	22.53
400C	0.53	56.96	3.08	0	13.78	22.41
500C	0.59	65.02	3.57	0	11.71	26.08
500C	0.49	61.1	3.03	0	12.36	23.94
600C	0.52	59.46	2.56	0	7.92	23.33
600C	0.48	60.44	2.5	0	4.93	23.91