

https://dspace.org/

Biofuel production from waste animal fat using pyrolysis (thermal cracking)

Obidike, Lawrence Ikechukwu

2016-10-11
http://hdl.handle.net/10539/21141

Downloaded from a DSpace repository. https://dspace.org/



BIOFUEL PRODUCTION FROM WASTE ANIMAL FAT USING PYROLYSIS (THERMAL CRACKING)

MSc RESEARCH DISSERTATION

Prepared by

Lawrence Ikechukwu Obidike

0312936W

Submitted to

School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, South Africa

Supervisor: Dr. Jean Mulopo

Co-Supervisor: Dr. Diakanua Nkazi

June, 2016

DECLARATION

I declare that this thesis is my own, unaided work. It is being submitted for the degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other university.

_____

Lawrence Ikechukwu OBIDIKE

June 2016

ABSTRACT

The main objective of this study is to produce biofuel from waste animal fat (collected from abattoirs) using the pyrolysis (thermal cracking) method. To achieve this goal, the study investigated the effects of temperature and heating rate on the yield and quality of the bio-oil produced. Also investigated was the effect of zeolite nano-catalyst(s) on the quality of the bio-oil produced.

Animal waste fat (tallow) was pyrolyzed in a laboratory fixed bed reactor of volume 2200 cm^3 at final temperatures (FT), 450^{o}C, 500^{o}C, 530^{o}C and 580^{o}C using heating rates (HR) of 4^{o}C/min, 5^{o}C/min and 6^{o}C/min. The properties of the resultant bio-oils were tested and analyzed. The maximum bio-oil yield of 82.78 % was achieved at 530^{o}C FT and 6^{o}C /min HR while the highest calorific value, 52.41 MJ/kg, was recorded from the bio-oil produced at the FT of 580^{o}C and 6^{o}C/min HR. The molecular components of each of the bio-oil samples was analyzed using the Gas Chromatography – Molecular Spectrograph (GC-MS) which indicated the predominant presence of alkanes, alkenes, carboxylic acids and alkyl esters in the bio-oils produced without a catalyst. The introduction of zeolites in nano-form yielded relatively more cyclo-alkanes and aromatics.

A maximum yield of 58% was recorded when 1% of the zeolite nano-catalyst was used to pyrolyse the tallow at 530^{o}C FT and 6^{o}C/min HR but with lots of coking and gas formation. The viscosity improved with a 35% reduction for the samples produced with 1% zeolites (C1 and C2). The viscosity of the bio-oil produced with 2% zeolites improved with a resultant 34% reduction in value. For pyrolysis done at 530^{o}C FT and 6^{o}C/min HR, the bio-oils with 1% (C1) and 2% zeolite (C3) resulted in a reduction in acid value of 32% and 30%, respectively. Acid value is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance.

ACKNOWLEDGMENT

I can do all things through Christ who gives me strength – Phil 4:13

I thank the Almighty God for His love that led me to start this programme and His strength that sustained me to complete it.

I express my profound respect and gratitude to my supervisor – *the best supervisor one could ask for*, Dr Jean Mulopo who provided me with insight, knowledge and all the support I needed to complete this research study.

I also thank my co-supervisor, Dr Diakanua Nkazi for his selfless contribution, guidance and support throughout this period of study.

I thank my friends and colleagues, Patrick Sekoai, Kevin Yoro, Masedi Mmonatau, Damilola McGregor, Ayotunde Awosusi and Ileshree Moodley for their eternal motivation and support throughout my study.

My profound appreciation to Dr Franklin Obazu for his encouraging words and guidance.

This work would not have been completed without the practical assistance of Mr Tapuwa Dzara and Mr Thapelo Mbhele of Wits Chemistry Department.

A special thanks to my family - my brother, Stanley who has been my pillar of support and continues to be my loudest cheerleader; my son, Chuka, who unknowingly, has been my greatest motivation in all I am doing (including this study).

This course of study probably would not have commenced without the persistent urging and practical support of my very dear friend, Felix "Baba" Obioha. To him, I owe a million thanks.

May the soul of my dearest mother, Bessie, who waited long enough for me to submit this dissertation before she passed on a few hours later, rest in the bosom of the Lord from whence it came.

LIST OF FIGURES

Figure 2.1: A mixture of animal waste dumped in the open---------- 5
Figure 2.2: Typical sources and uses of wastes in a red meat ---------- 6
Figure 2.3: Animal waste dumped near a river in Kaloor, India---------- 9
Figure 2.4: Molecular components of pyrolysis products ----------18
Figure 2.5: Schematic diagram of the pyrolysis process ---------- 19
Figure 2.6: Effect of final temperature on pyrolysis products of lamb fatty wastes ---------- 20
Figure 2.7: The effect of heating rate on pyrolysis products of lamb fatty wastes----------21
Figure 2.8. Effects of residence time on liquid yield of lard pyrolysis----------22
Figure 2.9: Fluidized Bed Reactor ----------24
Figure 2.10: Ablative Reactor ----------25
Figure 2.11: Basic Zeolite structure ---------- 35
Figure 2.12: The benefits of nano-catalysis ---------- 39
Figure 3.1 The ELITE reactor Temperature Controller (PID)---------- 43
Figure 3.2 Fat samples in silica boats about to be placed inside the reactor---------- 44
Figure 3.3 The pyrolysis experiment in progress ---------- 45
Figure 3.4 The zeolite powder used in the pyrolysis and its container---------- 46
Figure 4.1 Yield of bio-oil using 4, 5 and 6^{o}C /min heating rates. ---------- 49
Figure 4.2 Yield of bio-char using 4, 5 and 6^{o}C /min heating rates. ---------- 50
Figure 4.3 Yield of bio-gas using 4, 5 and 6^{o}C /min heating rates. ---------- 51
Figure 4.4 Bio-oil Yield at different Final Temperatures---------- 52
Figure 4.5 Biochar Yield at different Final Temperatures ---------- 53
Figure 4.6 Calorific Value of Bio-oil at 4, 5, and 6^{o}C/min HR ---------- 57
Figure 4.7 Density of Bio-oil at 4, 5, and 6^{o}C/min HR ---------- 58
Figure 4.8 Acid Values of Bio-oil at 4, 5, and 6^{o}C/min HR ---------- 59
Figure 4.9 Ash Content of Bio-oil at 4, 5, and 6^{o}C/min HR ---------- 60
Figure 4.10 Viscosity of the Bio-oils at 4, 5, and 6^{o}C/min HR ---------- 61
Figure 4.11 Acid Value of Bio-oils of B6 and C2 produced at 500^{o}C and 6^{o}C/min ---------- 63
Figure 4.12 Acid Value of Bio-oils of B9, C1 & C3 produced at 530^{o}C and 6^{o}C/min -------- 63
Figure 4.13 Viscosity of Bio-oils of B6 & C2 produced at 500^{o}C and 6^{o}C/min ---------- 64

Figure 4.14 Viscosity of Bio-oils of B9, C1 & C3 produced at 530^{o}C and 6^{o}C/min ---------- 65
Figure 4.15 Diepsloot ---------- 68

LIST OF TABLES

Table 2.1 Wastes Generated Per Cow and Goat ----------7

Table 2.2 South African Abattoir Waste Water Effluent ---------- 7

Table 2.3 Destination of Abattoir Waste in Developing Countries ---------- 8

Table 2.4 Oil and fat feedstock distribution in ten developed countries with self-sufficiency potential in 2006 ---------- 11

Table 2.5 Average composition of fatty acids in tallow ---------- 12

Table 2.6 Technical properties of biodiesel ---------- 12

Table 2.7 South Africa Automotive Diesel Fuel Specification ---------- 13

Table 2.8 Biodiesel (B100) specifications - ASTM D 6751 – 02 requirements ---------- 14

Table 2.9 Typical properties of wood pyrolysis bio-oil and of heavy fuel oil ---------- 27

Table 2.10 Characteristics of bio-oil ---------- 30

Table 2.11 Comparative efficiency of homogeneous, heterogeneous and nanocatalysis ---- 38

Table 3.1 Control parameters for the pyrolysis experiments without a catalyst ---------- 44

Table 4.1 Properties of the tallow feedstock ---------- 47

Table 4.2 Molecular composition of the fat feedstock ---------- 48

Table 4.3 The result of the pyrolysis experiments done without a catalyst ---------- 59

Table 4.4 The most occurring alkyl esters in the bio-oils produced without a catalyst ----- 54

Table 4.5 Properties of the pyrolysis bio-oil samples ---------- 56

Table 4.6 The result of the pyrolysis experiments with Zeolite nano-catalyst.---------- 62

Table 4.7 Properties of the samples of the pyrolysis with zeolite catalyst. ---------- 62

Table 4.8 Methyl esters of significant concentration in bio-oils produced with a catalyst - 66

NOMENCLATURE

Al_2O_3	Aluminium oxide
ASR	Automobile Shredder Residue
ASTM	American Society for Testing and Materials
BOD	Biochemical Oxygen Demand
BRICS	Brazil, Russia, India, China and South Africa
BSE	Bovine Spongiform Encephalopathy
CEF	Central Energy Fund
CFPP	Cold Filter Plugging Point
CH_4	Methane
CO	Carbon Monoxide
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
cSt	Centistokes (equivalent to mm^2/s)
CV	Calorific Value
DARD	Department of Agriculture and Rural Development
DEA	Department of Environmental Affairs
DEAT	Department of Environmental Affairs and Tourism
DME	Department of Minerals and Energy
EDC	Energy Development Corporation
EU	European Union
FAME	Fatty Acid Methyl Ester
FCC	Fluid Catalytic Cracking
FT	Final Temperature
H_2	Hydrogen
HHV	High Heating Value
H_2O	Water
HR	Heating Rate
IEA	International Energy Agency
MgO	Magnesium Oxide

MPa	MegaPascal
MSA	Meat Safety Act, 2000 (Act No. 40 of 2000)
NBIS	National Biofuels Industrial Strategy
NEMA	National Environmental Management Act
NiMo	Nickel-Molybdenum
NP	Nanoparticle
NWA	National Water Act, 1998 (Act No. 36 of 1998)
pH	Potency of Hydrogen
RMAA	Red Meat Abattoir Association
SiO_2	Silicon Dioxide
TDS	Total Dissolved Solids
TSS	Total Soluble Solids
USDA	United States Drug Agency

TABLE OF CONTENTS

DECLARATION ---------- **i**

ABSTRACT ----------**ii**

ACKNOWLEDGMENT ---------- **iii**

LIST OF FIGURES ---------- **iv**

LIST OF TABLES ---------- **vi**

NPOMENCLATURE ---------- **vii**

RESEARCH OUTPUT ---------- **ix**

CHAPTER 1: Introduction

1.1 Background and Motivations ---------- 1

1.2 Research Problem Statement ---------- 3

1.3 Research Questions ---------- 4

1.4 Research Objectives ---------- 4

CHAPTER 2: Literature Review

2.1 Abattoir Waste ---------- 5

2.2 Disposal of Abattoir Wastes in South Africa ---------- 7

2.3 Energy Use in Abattoirs ---------- 9

2.4 Biofuels ---------- 10

2.4.1 Biofuels as alternative fuel source ---------- 10

2.4.2 Sources of biomass for biofuel ---------- 10

2.4.3 Animal fat as a biomass ---------- 11

2.5 Biodiesel ---------- 12

2.6 Advantages Of Biofuel Over Fossil Fuel ---------- 14

2.7 Disadvantages Of Biodiesel Over Fossil Fuel ---------- 15

2.8 Renewable Energy Progress In South Africa ---------- 15

2.9 Pyrolysis ---------- 17

2.10 Factors That Affect Pyrolysis Yield ---------- 20

2.10.1 Final temperature ---------- 20

2.10.2 Heating rate ---------- 21

2.10.3 Residence time ---------- 22
2.10.4 Type of reactor ---------- 23
a. Fixed-bed reactor ---------- 23
b. Fluidized-bed reactor ---------- 24
c. Ablative reactor ---------- 25
2.10.5 Feedstock ---------- 25
2.11 Advantages Of Pyrolysis Over Trans-Esterification ---------- 26
2.12 Products Of Pyrolysis ---------- 27
2.12.1 Bio-oil ---------- 27
a. Water ---------- 28
b. Oxygen ---------- 28
c. Viscosity ---------- 28
d. Acidity ---------- 29
e. Heating value ---------- 29
f. Ash ---------- 29
2.13 Bio-Char ---------- 32
2.14 Bio-Gas ---------- 33
2.15 Catalysis In The Pyrolysis Of Fats ---------- 33
2.15.1 Transition metal catalysts ---------- 33
2.15.2 Molecular sieve catalysts ---------- 34
2.15.3 Advantages of Zeolite as a Catalyst ---------- 36
2.15.4 Activated alumina ---------- 36
2.15.5 Sodium carbonate ---------- 37
2.16 Nano-Catalysis ---------- 37
2.17 Benefits of nano-catalysis ---------- 39
2.18 Sodium Silicate As A Nano-Catalyst In The Pyrolysis Of Fat ---------- 39

CHAPTER 3: Materials and Methods

3.1 Materials ---------- 40
3.2 Tests to characterize raw materials and products ---------- 40

3.2.1 CHNS-O elemental content ---------- 40
3.2.2 Acid value ---------- 41
3.2.3 Ash content ---------- 41
3.2.4 pH ---------- 41
3.2.5 Density ---------- 41
3.2.6 Calorific value ---------- 42
3.2.7 Mass Spectrometry-Gas Chromatography (GC–MS) ---------- 42
3.2.8 Viscosity ---------- 42
3.2.9 X-Ray Diffraction ---------- 42
3.3 METHODS
3.3.1 Pyrolysis Experimental Set Up And Procedure ---------- 42

CHAPTER 4: The Effect of Temperature and Heating Rate on Yield in the Pyrolysis of Tallow

4.1 Results and discussion ---------- 48
4.2.1 Properties of the beef fat (tallow) used in the pyrolysis ---------- 48
4.2 Pyrolysis experiments without a catalyst ---------- 49
4.2.1 Effect of temperature on yield ---------- 50
4.2.2 Effect of heating rate on yield ---------- 53
4.2.3 Bio-char ---------- 54
4.2.4 Fatty acid methyl esters ---------- 54
4.2.5 Analysis of bio-oils properties ---------- 57
4.3 Effect of Zeolite Catalyst on the Pyrolysis Experiment ---------- 63
4.4 Assessment Of Some Of The Economic Impact Of Bio-Oil Production From Abattoir Waste ---------- 67

CHAPTER 5: Conclusion and Recommendations

5.1 Conclusion ---------- 72
5.2 Recommendations for future work ---------- 72

REFERENCES ---------- 73
APPENDIX: Research Output ---------- 98

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND AND MOTIVATION

The rising global population and economic growth has led to increased demand for protein, corresponding to increased production, and slaughter of game and livestock animals (usually in abattoirs). In 2010, global meat production was 237.7 million tons, of which 42.7%, 33.4%, 23.9% were pork, poultry and beef respectively (USDA, 2010). In South Africa, about 436 620 animals, consisting of 45,360 cattle, 275 439 sheep, and 115 674 goats were slaughtered in 2006, (DEAT, 2007). In 2013, the figure was 9 million, of sheep (5 million), pigs (2 million) and cattle (2 million), in the 479 registered abattoirs in the country (Neethling, 2014). Between November 2013 and October 2014, 9 725 299 animals of sheep (4 841 475), pig (2 461 235) and cattle (2 422 589) were slaughtered (Neethling, 2014). This figure excludes other livestock like chicken, ostrich, crocodile, horse, etc.

Among the five major emerging national economies of BRICS – Brazil, Russia, India, China and South Africa, the gross national per capita income of China grew annually at 13.44% between 2000 and 2010. Correspondingly, China's meat consumption equally grew annually at 2.3% (12.7 million tons) in that period. In India, per capita income growth of 9.23% over the same period led to a 6.68% per year (2.2 million tons) increase in meat consumption. Brazil's 5.22% growth from 2000 to 2009 led to an increase in meat consumption of +3.64% per year (4.8 million tons). A similar phenomenon was observed in Russia where meat consumption grew 5.07% per year (3 million tons) between 2000 and 2009 (Feddern et al., 2011).

The process of converting these animals to meat, in an abattoir, unavoidably produces a sizable amount of waste, especially fat. The South African Department of Agriculture and Rural Development (DARD) defines an abattoir as any registered facility that is responsible for the conversion of animals to meat via a slaughtering process (DARD, 2009). Bovine produces approximately 31kg of solid waste - rumen content, faecal material (manure), condemned material, feather, fur, skins, horns and hooves, and bones, and 818 litres of liquid waste - blood, bile, urine, dissolved detergents, chemicals and waste water (Neethling, 2014). The waste water contains high organic matter, biological nutrients and has alkalinity. Blood constitutes the

highest pollution load and highest Chemical Oxygen Demand (COD) of all the components of liquid effluents, followed by fat (Chukwu, Adeoye and Chidiebere, 2011). Overwhelmed by this huge amount of waste, most abattoirs, especially in developing countries, (including South Africa) dispose of them by resorting to environmentally- harmful methods like incineration, spraying and burying. Others discharge their waste material in nearby streams and ponds, methods which are unhygienic and dangerous to human health. This also contributes to high organic and nutrient loads in streams that leads to eutrophication and compromise fresh water life (Muchenje et al., 2013).

Some abattoirs have discovered an clever way of disposing their waste mixture of fat and other trimmings. They pretreat this bulk waste with sodium hydroxide in an inadvertent saponification process to produce a soap-like mass which is then disposed into a stream.. This "soap-like" mass slowly dissolves in the stream as it moves along, leaving little residual trace but is harmful to organisms living within the water. Additionally, sodium hydroxide is expensive, and added to the cost of hiring a waste disposal company, the total expenditure incurred in disposing this waste becomes prohibitive.

In South Africa, the management of abattoir waste is regulated through the National Environmental Management Act, 1998 (Act 107 of 1998) (NEMA), the National Water Act, 1998 (Act. 36 of 1998) (NWA), the MSA and sections 24a and 24b of the Constitution of South Africa, 1996. In 1989, the abattoir industry consumed about 21% (5.8 million cubic metres) of the national water budget (Neethling, 2014) and generally has difficulty in meeting municipal quality standards by-laws for fats, oils, greases and suspended solids. About 84% of this water (4.87 million cubic metres) was discharged as wastewater effluent (DARD, 2009). According to an estimate by the Water Research Commission, discharge costs due to these high organic loads amounts to R21.33 million per year at R4.38/m^3. Also, these wastes pose great human danger through food contamination when eaten by scavengers or persons living off refuse sites.

However, energy security is regarded as one of the greatest threats facing humanity presently, coupled with anthropogenic climate change (McCartney, Hanlon, and Romanes, 2008). Studies confirm that oil reserves have been declining since the 1960s due to high demand and overuse in developed countries. It is estimated that the global oil supply will be less than 10 gigabarrels per

annum in 2015 and with the current global energy consumption approaching 1 gigabarrel per annum (BP, 2013), a looming energy crisis must be averted. Presently, more than 80% of global primary energy is derived from fossil fuels with oil accounting for 32.8%, coal, 27.2% and natural gas, 20.9% (IEA, 2011).

Studies indicate that the major greenhouse gases are carbon dioxide, methane, nitrous oxide and halocarbons respectively with carbon dioxide regarded as the most abundant anthropogenic greenhouse gas in the atmosphere, and the main contributor to climate change (Stern, 2008). It is produced from the combustion of fossil fuel reserves with 62% released into the atmosphere every year. While other studies show that CO_2 levels have increased to 390 ppm since 2007 (Tans and Keeling, 2011), the International Energy Agency predicted that 30 billion tons of CO_2 were emitted from fossil fuels in 2008 (IEA, 2011). Climatologists have predicted that if no actions are taken, the levels of CO_2 in the atmosphere could increase to 560 ppm by 2035 with an atmospheric temperature rise exceeding 5 °C (Stern, 2008), and exacerbating the ongoing global warming. This could lead millions of people to poverty, warns the World Bank (2013).

Therefore, an urgent need arises to promote the development of alternative green fuels in order to meet the escalating global energy demand and also reduce carbon emissions.

1.2 RESEARCH PROBLEM STATEMENT

Since the traditional methods of abattoirs wastes' disposal have become obsolete, and the chosen method of first saponifying the fat before disposal is both costly and environmentally harmful, South Africa is bound, as a signatory to the Basel Convention (UNEP, 2000) on waste disposal, to find alternative methods of waste disposal that are healthy to humans and conducive to the environment. One of the most economical benefits of waste animal fat may be their conversion into biofuel in order to generate energy and reduce the abattoir's power demand on the national grid especially with the prevalent load-shedding presently in South Africa. This will equally reduce the pollution level of the waste water effluent. This research aims to assess the potential of converting animal waste fat into biofuel using the pyrolysis (thermal treatment) method.

1.3 RESEARCH QUESTIONS

This research aims to address the following questions:

a. What is the optimal heating rate and temperature for the production of bio-oil from waste animal fat?
b. Could the quality of the bio-oil derived from the pyrolysis of waste animal fat match those of the fossil fuels?
c. Will the quantity of waste fat derived by each abattoir yield enough biofuel to satisfy their energy demand in order to make this process economically viable for them?
d. Could the properties of the bio-oil derived from the pyrolysis of waste animal fat be improved by a suitable nano-catalyst?
e. Could the nano-catalyst improve the pyrolysis process by reducing the operating temperature of the process thus reducing the energy input into the process?

1.4 RESEARCH OBJECTIVES:

The main objective of this study is to produce biofuel from waste animal fat from abattoirs using the pyrolysis (thermal treatment) method. To achieve this goal, the following objectives will be investigated:

a. The potential for production of bio-oil from waste animal fat using the pyrolysis method.
b. The effects of temperature and heating rate on the yield and quality of the bio-oil produced.
c. The effects of zeolite nano-catalyst on the quality of the bio-oil produced.
d. The effects of zeolite nano-catalyst on the temperature of the pyrolysis process.

CHAPTER 2: LITERATURE REVIEW

2.1 ABATTOIR WASTE



Figure 2.1 A mixture of animal waste dumped in the open (http://forum.hardware.fr)

Waste management includes the generation, storage, transport, treatment and the ultimate disposal of all types of waste streams (DARD, 2009). South Africa has been experiencing a rapid increase in animal wastes due to increased demand for animal protein. From September 1990, the South African government banned the use of meat-and-bone meal derived from the brain, spinal cord, thymus, spleen, tonsils and intestines of bovine offal because they are believed to be the tissues most likely to contain the agent that causes Bovine Spongiform Encephalopathy, (BSE) or "mad cow disease" (DARD, 2009). This embargo increased the amount of waste from abattoirs, further compounding the waste disposal quandary abattoirs faced. Of the 59 million tons of general waste generated in South Africa in 2011, 2.95, 7.88 and 12.1 million tons were estimated to have emanated from agricultural, municipal and industrial process effluents respectively (DEA, 2012).This quantity is expected to increase in subsequent years due to

urbanization and industrialization in most cities across the country (DEA, 2012). Considering the amount of residues produced by abattoirs - 45% (wt/wt) for cattle and 25% (wt/wt) for swine and poultry, they contain approximately 15% fat (Feddern et al. 2011).

Globally, about 27.9 million metric tons per year of waste animal fat is produced (Gunstone, 2001).

South Africa has 604 registered abattoirs (Neethling, 2014) that produce about 400 billion tonnes of solid waste per year (Kruger, 2013) and which excludes blood, fat and other liquid wastes.

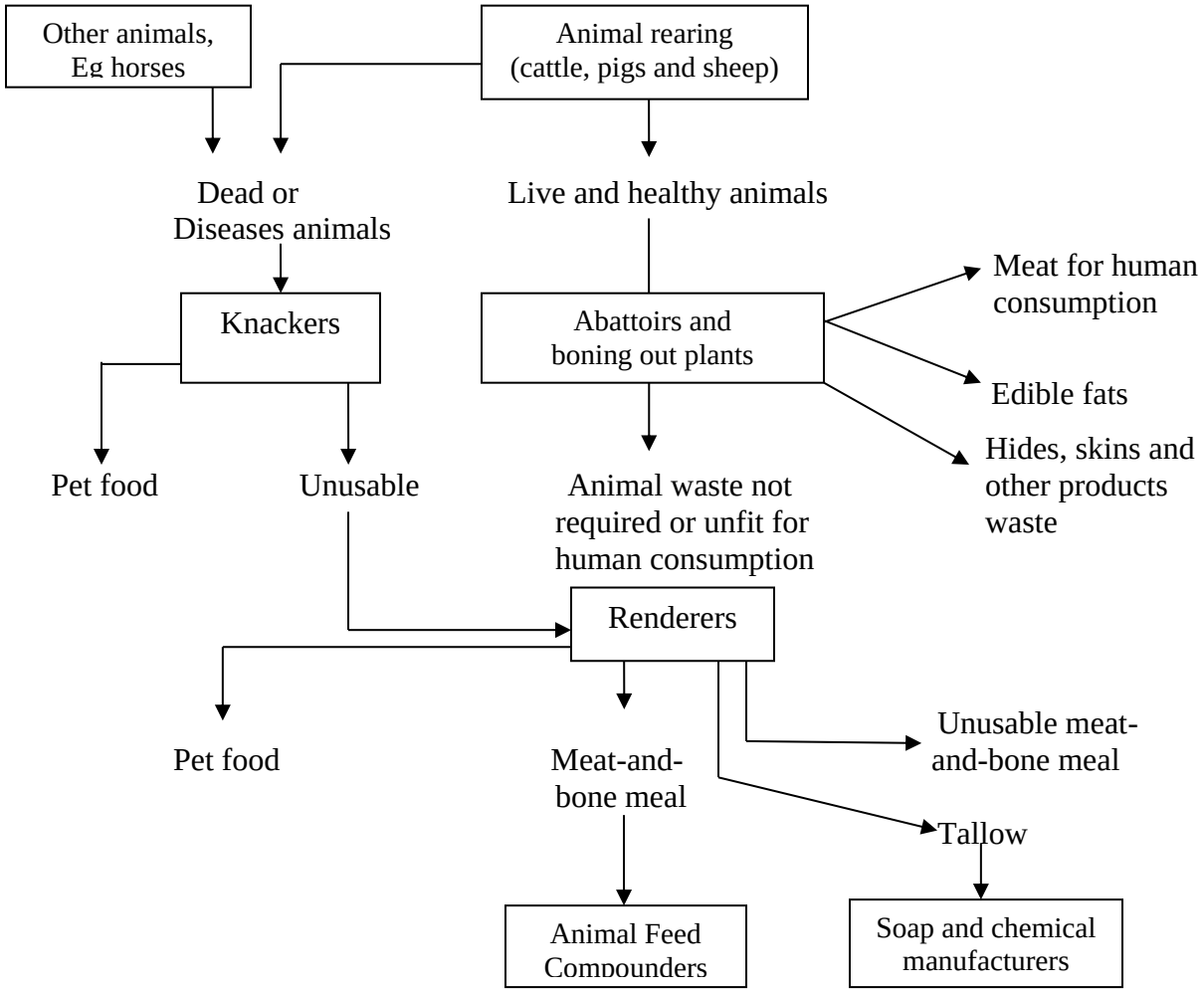


Figure 2.2 Typical sources and uses of wastes in a red meat abattoir (DARD, 2009)

Table 2.1 Wastes Generated Per Cow & Goat (Aniebo et al, 2011)

	Cow	Goat
Blood/head (kg)	12.6	0.72
Intestinal content/head (kg)	8.0	1.25
Waste tissue/head (kg)	6.4	0.8
Bone/head (kg)	11.8	2.06

2.2 DISPOSAL OF ABATTOIR WASTES IN SOUTH AFRICA

Pollution control and environmental protection are vitally important in the disposal of abattoir wastes hence rendering is the main disposal method. It involves a series of drying and separating processes by which the material is sterilised and the fats and proteins are extracted to produce tallow, blood and meat-and-bone meal. Water from the waste material needs to be treated to avoid pollution before being removed. The organic nature of the material causes odour pollution that requires additional pollution abatement technology. Below is a comparison of a South African abattoir waste water effluent against the municipality requirement:

Table 2.2 South African Abattoir Waste Water Effluent (DARD, 2009)

	Abattoir Effluent	Municipality Requirement
pH	5.7 – 8.4	6 - 10
Chemical Oxygen Demand (COD)	2380 – 8942 mg	3000 - 5000
Total Dissolved Solids (TDS)	595 – 2805 mg/L	500 mg/L (TSS)
Suspended Matter	189 – 3330mg/L	
Total Kjedahl Nitrogen	0.71 – 24 mg/L	200 – 300 mg/L

The main technical alternatives to rendering are landfill, incineration and anaerobic digestion. Only small amounts of animal waste are currently disposed of to landfill because of the legal requirement that stipulates that abattoir wastes must be adequately sterilised before disposal to landfill. Only a few sites are licensed for this. Incineration appears to be more suitable for dealing with whole carcasses than for waste offal, which has high water content and low calorific

value but the costs of incineration are relatively high. Consequently, it is being phased out throughout South Africa as government generally does not support it (DARD, 2009).

Anaerobic digestion is a process whereby organic material such as animal waste is broken down by micro-organisms operating in an oxygen-free environment. The costs are more uncertain than for other forms of waste treatment and disposal, and the technology for handling abattoir wastes is still in the process of development. Developments in this area show considerable promise as both a low-cost and low-pollution means of dealing with raw animal and other waste, although these newer technologies have yet to be fully tested and commercially proven (DARD, 2009).

Table 2.3 Destination of Abattoir Waste in Developing Countries (World Bank Study, 2008)

LOCATION	**WASTES**	**DESTINATION IN DEVELOPING COUNTRIES**
Livestock Holding Area	Bedding, Straw, Truck waste, Dead-stock	Formal and informal landfill, Composting
Stunning & Bleeding	Blood	Collected as edible or Processed into Protein meal, or Discharged in wastewater
Dressing	Heads, Hooves, Feet	Recovered as edible products
	Hide, Feathers	Recovered for further processing into leather, protein meal, etc
	Horns, Pig Hair	Often disposed to landfill
Evisceration, Splitting & Trimming	Trimmings & Fat	Recovered as edible products
Inspection	Pathological material	Little produced in most countries. Goes to landfill, compost, incineration
Edible Offal Processing	Trimmings	Recovered as edible products
Intestinal Offal Processing	Trimmings	Recovered as edible products
	Stomach & Intestinal Contents	Formal and informal landfill, Composting, Fish feed
Wastewater	Contamination with blood, body fluids and intestinal contents	Mostly discharged direct to surface water without any treatment (even screening), occasionally to the Municipal sewer.



Figure 2.3 Animal waste dumped near a river in Kaloor, India. (Express News Service, 2015)

2.3 ENERGY USE IN ABATTOIRS

According to the Agriculture and Horticulture Development Board (AHDB), the cost of energy represents the fourth highest operational cost for many meat plants, after the cost of raw materials, waste disposal and labour (AHDB, 2013). This has increased because plants have increased their level of processing, yet few companies know how energy is distributed within their plants.

A study by AHDB (2013) has shown that typically 50–80% of energy used in an abattoir is provided by electricity while the other 20–50% comes from thermal energy. Electricity is usually used for refrigeration and compressed air, ventilation, lighting, powering the operating equipment in the slaughter, boning and by-product processing areas, e.g. saws, hoists, conveyors, packing machines, and electrical stimulation.

Studies show that it takes about 775 kWh of energy to produce a tonne of beef and 685 kWh per tonne of sheep meat based on the energy used for slaughtering, cutting and retail packing,

although the energy per tonne varied considerably depending upon the type of processes within the plant. At 'slaughter only' abattoirs for example, the electricity average per head was measured at 50 kWh (with a range of 16 to 67) and the total energy use averaged 96 kWh per tonne (range 47 to 189).

2.4 BIOFUELS

2.4.1 Biofuels As Alternative Fuel Source

With increasing energy consumption, populations and economic developments, and worsened by a progressive exhaustion of limited fossil fuels, renewable energy has been widely explored in order to replenish the energy sources structure and keep sustainable development safe (Qi et al, 2006). Biomass is an attractive supplement to fossil fuels because it has negligible content of sulphur, nitrogen and ash, which give lower emissions of SO_2, NO_x and soot than conventional fossil fuels (Qi et al, 2006). Compared to other renewable energy sources, biomass is the most interesting one since it can be converted directly into liquid, gaseous and solid fuels, usable for transport, heat and power production (Bridgwater and Peacocke, 2000)

2.4.2 Sources Of Biomass For Biofuel

Karaosmanoglu, Tetik, and Gollu (1999) define biomass as encompassing all natural matter of vegetables and animals and can include a variety of natural and derived materials while Klass (2004) described it as all non-fossil based living and dead organisms and organic materials that have intrinsic chemical energy content. Many biomass species have been pyrolyzed, such as almond shell, apple pulp, apricot stones, automobile shredder residue (ASR), bagasse, beech wood, cellulose, corn–potato starch gel, corn stalk, cotton stalk, extracted oil palm fibers, filter pulp, grape, grass, ground nut shell, maize, etc. (Yaman, 2003). The main commodities for biodiesel production from inedible oils, which are recommended as they are more economical than edible oils are plant species such as jatropha, ratanjyote, seemaikattamankku (J. curcas), karanja, honge (P. pinnata), nagchampa (C. inophyllum), rubber seed tree (Hevca brasiliensis), neem (Azadirachta indica), mahua (M. indica and Madhuca longifolia), silk cotton tree (Ceiba pentandra), jojoba (Simmondsia chinensis), babassu tree, Euphorbia tirucalli, and microalgae (Demirbas, 2009).

2.4.3 Animal Fat As a Biomass

Fat is one of the sources of biomass. Oils and fats are found in living organisms, consisting essentially of fatty acid esters and glycerin mixtures, and are known as triacylglycerols or triglycerides (Feddern et al. 2011). These triacylglycerols have higher viscosity and therefore cannot be used as fuel in common diesel engines (ibid) but will need to be refined to conform to diesel properties. Technologies such as biochemical, thermo-chemical, physical and chemical processes are available for recovering bio-fuels from triglyceride based materials. Thermo-chemical processes include gasification, pyrolysis and combustion (Bridgwater, 2003). Among these technologies, pyrolysis is favoured because it is simple and inexpensive to construct (Onay and Kockar, 2004).

Table 2.4 Oil and fat feedstock distribution in ten developed countries with self-sufficiency potential in 2006 (Demirbas, 2009)

Feedstock	**%**
Animal fats	52
Soybean oil	20
Rapeseed oil	11
Palm oil	6
Sunflower oil	5
Other vegetable oils	5

Beef fat, called tallow, is a mixture of triglycerides, most of which are saturated of which tristearin is usually the major component (Ma & Hanna, 1999). These saturated fatty acid components in tallow accounts for almost 50% of the total fatty acids. The higher palmitic and stearic acid contents endow tallow with its unique properties of high melting point and high viscosity (Demirbas, 2009). Table 2.5 shows the average composition of fatty acids in tallow (Demirbas, 2008). The total fatty acids in the tallow samples were 51.1% by weight. The major fatty acids in the tallow were palmitic (28.7%), stearic (19.5), and oleic (44.4%) acids. Higher palmitic and stearic acid contents give the tallow a high melting point (Demirbas, 2008).

Table 2.5 Average composition of fatty acids in tallow (Demirbas, 2009)

Fatty acid	wt%
Myristic (14:0)	2.90
Palmitic (16:0)	28.70
Stearic (18:0)	19.50
Oleic (18:1)	44.40
Linoleic (18:2)	3.60
Linolenic (18:3)	0.90

2.5 BIODIESEL

Bio-diesel is formally defined as "a fuel comprising of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100" (ASTM D 6751-03a, 2005). In USA and Europe, soybean oil and rapeseed oil respectively are the major feedstock for biodiesel production, but in the East Asian countries, where production was 31.4 million tons/year between 2006 and 2010 (Feddern et al, 2011), it is palm oil (Shrestha & Gerpen, 2010).

Table 2.6 Technical properties of biodiesel (Demirbas, 2009)

Common name	Biodiesel (bio-diesel)
Common chemical name	Fatty acid (m)ethyl ester
Chemical formula range	C_{14}–C_{24} methyl esters or $C_{15\text{-}25}H_{28\text{-}48}O_2$
Kinematic viscosity range (mm^2/s, at 40 ^oC)	3.3–5.2
Density range (kg/m^3, at 15 ^oC)	860–894
Boiling point range (^oC)	>272
Flash point range (^oC)	147–177
Distillation range (^oC)	197–327
Vapor pressure (mm Hg, at 22 ^oC)	<5
Solubility in water	Insoluble in water
Physical appearance	Light to dark yellow, clear liquid
Odor	Light musty/soapy odor
Biodegradability	More biodegradable than petroleum diesel
Reactivity	Stable, but avoid strong oxidizing agents

Brazil produced 2.4 billion litres of biodiesel in 2010, which is 14% of the year's global production but Germany produces half of the EU output (Feddern et al, 2011). In 2007, European Union (EU) produced 5.7 million tons of biodiesel and USA production hit 1.7 billion litres (Feddern et al, 2011).

Bio-diesel is primarily used as a substitute or blend for diesel fuel, but it can also be used as a feedstock in the chemical industry. It is utilized in farm equipment and military vehicles (National Biodiesel Board, 2005). Biodiesel also can have application as non-ionic surfactants or as emulsifying, thickening and plastifying agents (Schuchardt et al., 1998).

Table 2.7 South Africa Automotive Diesel Fuel Specification (SAPIA, 2008)

Property	Units	Limit	SANS 342 - 2006
Appearance		max	
Colour	max		
Density @ 20 °C	kg/l	min	0,8000
Ash Content	% m/m	max	0,01
Cetane Number		min	45
Carbon Residue, Ramsbottom (on 10 % residue)	% m/m	max	0,2
CFPP – Winter – Summer			-4 3
Corrosion, Copper Strip, 3 hrs @ 100 °C		max	1
Distillation (90% vol. Recovery)	Deg C	max	362
Sulphur Content	mg/kg	max	500
Flash point, PMCC	Deg C	min	55
Kinematic Viscosity @ 40 ^{o}C	cSt	min	2.2
		max	5.3
Water Content, Karl Fischer	ppm (v/v)	max	500
Total Contamination	mg/kg	max	24
Lubricity Wear scar diameter	um	max	460
Oxidation Stability	mg/100ml	max	2.0
Fatty Acid Methyl Ester (FAME) content	vol %	max	5

ASTM D 6751 is a standard that identifies the parameters pure biodiesel (B100) must meet before being used as a pure fuel or being blended with petroleum-based diesel fuel. Biodiesel, B100, specifications (ASTM D 6751 – 02 requirements) are given in Table 2.8.

Table 2.8 Biodiesel (B100) spec. - ASTM D 6751 – 02 requirements (Demirbas, 2009)

Property	Method	Limits	Units
Flash point	D 93	130 min	^{o}C
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity at 40 ^{o}C	D 445	1.9–6.0	mm2/s
Sulfated ash	D 874	0.020 max	wt%
Total sulfur	D 5453	0.05 max	wt%
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report	^{o}C
Carbon residue	D 4530	0.050 max	wt%
Acid number	D 664	0.80 max	mg KOH/g
Free glycerine	D 6584	0.020	wt%
Total glycerine	D 6584	0.240	wt%
Phosphorus	D 4951	0.0010	wt%
Vacuum distillation end point	D 1160	360 _C max, at 90% distilled	^{o}C

2.6 ADVANTAGES OF BIOFUEL OVER FOSSIL FUEL

- Bio-diesel easily meets the cetane requirement for diesels, an indicator of diesel combustion and quality, and can be used in a regular diesel engine with little or no modification.
- Many harmful emissions, which are a major concern of fossil fuel combustion, are reduced.
- Bio-diesel exhibits superior lubricity to conventional diesel. Lubricity has become significant because the new low sulfur diesels, required for regulatory reasons, exhibit low lubricity resulting in failure of fuel injectors and pumps (Knothe and Steidley, 2005).
- Bio-diesel has a net positive energy balance. Life-cycle analysis of bio-diesel has shown that approximately 3.2 units of fossil energy are generated for every unit of fossil energy used to produce the fuel (Sheehan et al., 1998).

- Other notable advantages of biodiesel over diesel fuel are its portability, ready availability, renewability, higher combustion efficiency, lower sulphur and aromatic content, higher biodegradability, safer handling, besides being non-toxic (Lapuerta et al., 2008).

2.7 DISADVANTAGES OF BIODIESEL OVER FOSSIL FUEL

- Bio-diesel exhibits poor cold flow properties, which can impact negatively on engine performance, and increase NOx emissions.
- Bio-diesel contains oxygen which may not be desirable for certain applications:
  a. The presence of oxygen can also cause stability problems and lowers the heat content; the heating values of bio-diesel is 9–13% lower than those of diesel fuels on a mass basis (Demirbas, 2003).
  b. Vegetable oil derivatives are prone to deterioration through hydrolytic and oxidative reactions.
- It causes higher copper strip corrosion.
- It creates fuel pumping difficulty due to its higher viscosity.
- Currently, biodiesel is more expensive to produce than diesel, which appears to be the primary factor in preventing its more widespread use.
- Current worldwide production of vegetable oil and animal fat is not enough to replace liquid fossil fuel use (Bala, 2005).

2.8 RENEWABLE ENERGY PROGRESS IN SOUTH AFRICA

In South Africa, progress in the biofuels industry has been very modest. The main driver for the development of the industry is neither the economic threat of erratically increasing oil prices nor a mitigation agenda for anthropogenic climate change, as obtained internationally. Instead, it is driven by the need to stimulate economic development and alleviate poverty by promoting farming in the areas that did not have market access for their produce, most of which are in the former homeland areas that were previously neglected by the apartheid system (Letete and von Blottnitz, DME 2007).

In 2007, the South Africa government released the National Biofuels Industrial Strategy (NBIS) proposing a five (5) year pilot of biofuels market penetration target of 2% of national liquid fuel

supply, or 400 million litres per year to be based on local agricultural and manufacturing production by 2013 (Letete and von Blottnitz, 2009; DME, 2007). The Strategy proposes to set a fixed margin price and offer a 100% petrol tax exemption for bioethanol, and 50% fuel levy exemption for biodiesel (Letete and von Blottnitz, 2009; DME, 2007). Energy Development Corporation (EDC), a division of the state-owned Central Energy Fund, is working with Sasol to study the feasibility of converting soya beans into 100-million litres of biofuel, mostly biodiesel, per year (SouthAfricaInfo, 2006).

At the 2009 Copenhagen climate conference, the South African government committed to reduce the country's carbon emissions by 34% and 42% by 2020 and 2025 respectively by substituting most of the 90% of power generation that came from coal-fired stations, which is responsible for half the country's carbon emission. Government hoped that this would be achieved by setting up the Independent Power Producer Programme – a transparent public-private partnership to develop renewable energy. It is estimated that through the Integrated Resource Plan 2010, renewable energy sources would supply 40% (18 000MW) of the country's power by 2030.

So far, sorghum and soy beans have been approved as the bioethanol and biodiesel feedstock respectively. Excluded from consideration are maize - for food security issues, and jatropha - an alien to South Africa with a very high calorific value of seed oil but which produces a toxic seedcake remnant after biofuels production (Gilder and Mamkeli, 2014). This consideration conforms to the United Nations World Water Development Report of 2014 which states that biofuels development needs to be considered in the context of food security, energy requirements, the availability of land and national priorities (Gilder and Mamkeli, 2014). With the failed initial target of implementing mandatory blending of biofuels with fossil fuels by 1 October 2015, a policy that would create up to 25 000 new jobs (Letete and von Blottnitz, 2009; DME, 2007), the government has granted eight companies provisional licenses to produce bioethanol or biodiesel in the country. Rainbow Nation Renewable Fuels Ltd plans to erect a 1.1 Mt/yr soybean crushing facility that will produce about 228 ML biodiesel (Gilder and Mamkeli, 2014) while Mabele Fuels is ready to start building a 158-million litre per year bio-ethanol refinery near Bothaville, Free State, with sorghum as its preferred feedstock once the regulations are finalized (Gilder and Mamkeli, 2014). Industrial Development Corporation (IDC) is planning to invest in at least five projects for the production of fuel-grade ethanol and has approved R3.2b

to build a bioethanol plant in Kwazulu Natal (South Africa Info, 2013). A solar plant outside De Aar in the Northern Cape created 2000 jobs during construction, and R1-million from the project went to black women in the area for the development of ostrich farms. Turbine production factories have been built in Cape Town and Port Elizabeth. Fuel firm, Ethanol Africa has announced a deal with Sterling Waterford to build the first of eight bioethanol plants in the Free State town of Bothaville - the heartland of South African maize production - at a cost of R700 million (ibid). They plan to further build a string of maize-to-ethanol plants in South Africa at a total cost of about $1-billion (about R6-billion), partly pegged on the hope that new laws could make its product mandatory (South Africa Info, 2013).

2.9 PYROLYSIS

Pyrolysis is regarded as one of the reasonable and promising technologies to compete with and eventually replace non-renewable fossil fuel resources (Qi et al, 2006). It is a thermo-chemical process in which organic materials are heated to temperatures greater than 400°C in the absence of oxygen to transform low-density biomass into a high-energy-density liquid known as bio-oil, a high-energy-density solid known as biochar, and a relatively low energy-density gas known as syngas (Bridgwater et al., 1999). Pyrolysis mechanisms of triglycerides were proposed by several authors (Chang and Wan, 1947; Alencer et al., 1983; Vonghia et al., 1995; Idem et al., 1996) who all postulated that elimination of heavy oxygenated hydrocarbons as esters, carboxylic acids, ketones, and aldehydes is a dominant step in the cracking reactions of triglycerides. At these temperatures, organic materials thermally decompose, with the long chains of carbon, hydrogen and oxygen compounds in the biomass breaking down into smaller molecules. This consists of both simultaneous and successive reactions. The pyrolysis vapor condenses out as liquid (bio-oil), a polar and high molecular-weight compounds while low-molecular-weight volatile compounds remain in the gas phase (syngas). The physics and chemistry occurring during a pyrolysis reaction are very complex and depend on both the nature of the biomass and the reactor conditions (Babu, 2008). The bio-oil yield could be as much as 70–80%.

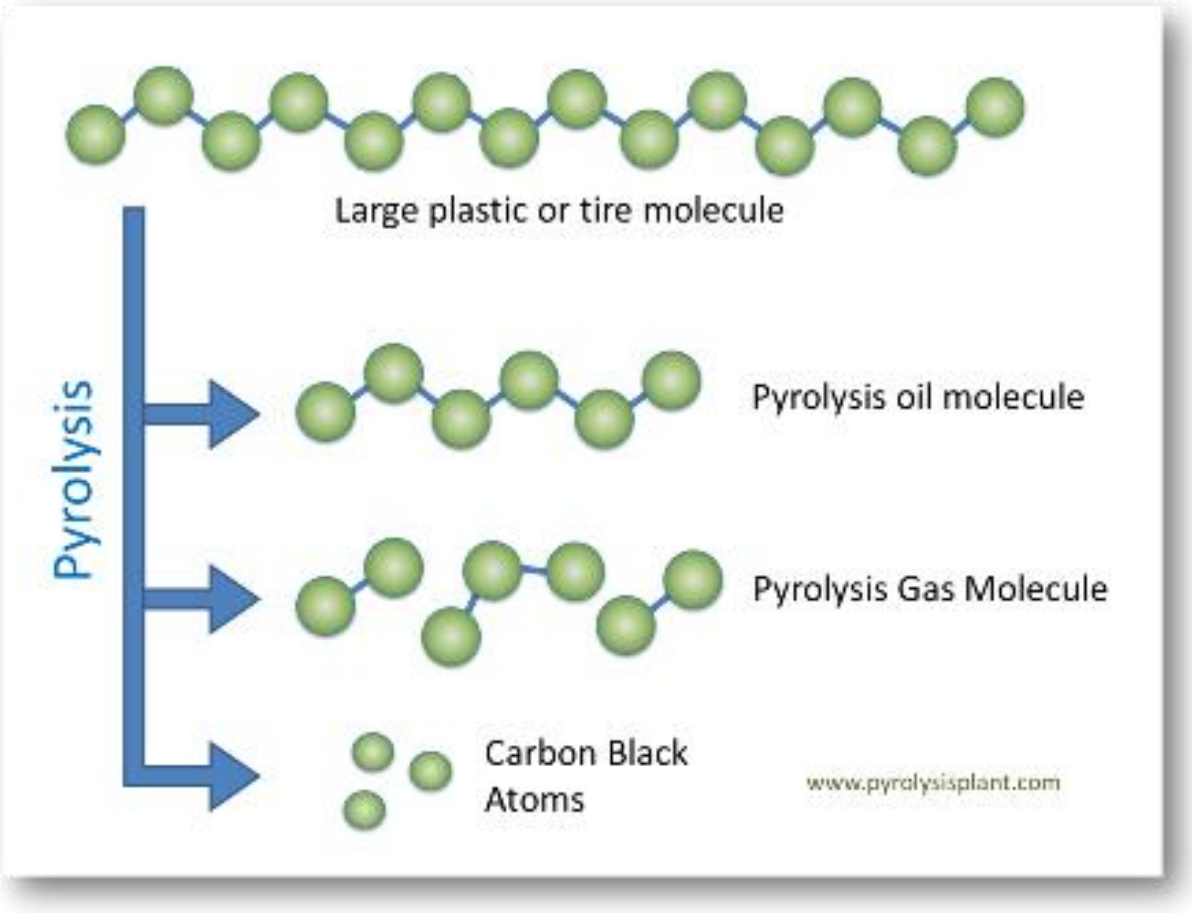


Figure 2.4 Molecular components of pyrolysis products (www.pyrolysisplant.com)

Pyrolysis can be classified into four general categories: slow pyrolysis, flash pyrolysis, gasification, and fast pyrolysis (Laird et al., 2009).

Slow pyrolyzers are either batch systems known as 'charcoal kilns', or continuous systems that slowly heat the biomass to >400°C. Moisture content and particle size are not critical for charcoal kilns while continuous systems do specify some size reduction and drying for optimal results. Product yields are approximately 35% biochar, 30% bio-oil, and 35% syngas by mass (Goyal et al., 2008) Typically, the bio-oil, in the form of vapors and aerosols, is not separated from the syngas.

Flash pyrolysis is designed to maximize biochar production. It involves the heating of biomass under moderate to high pressure. Its yields are typically 60% biochar and 40% volatiles (bio-oil

and syngas). Flash pyrolyzers are more likely to include heat-recovery equipment than traditional kilns (Laird et al., 2009).

Gasification is designed to maximize production of syngas. A typical gasifier allows a small, controlled amount of oxygen into the reaction chamber which causes partial combustion of the biomass, and generates the heat needed to sustain the reaction. The reaction temperature is generally quite high, about 800–1200°C (ibid). A gasifier produces very little char or bio-oil although many commercial gasifiers can produce 5–15% char and traces of bio-oil, which is referred to as 'tar' (Laird et al., 2009).

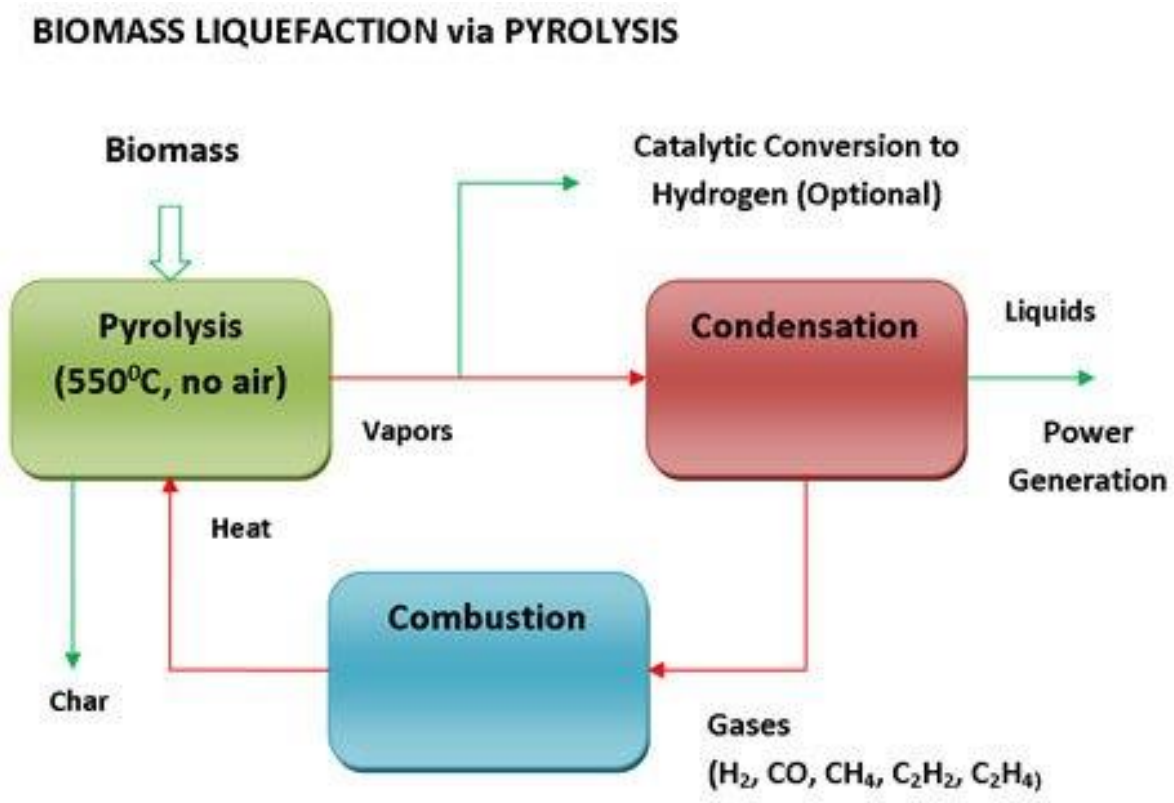


Figure 2.5 Schematic diagram of the pyrolysis process

Fast pyrolyzers are continuous flow systems designed to maximize production of bio-oil. The biomass must first be dried to <10% water content and ground to <2 mm particle size before entering a fast pyrolyzer. The product yields by mass are typically 50–70% bio-oil, 10–30% biochar, and 15–20% syngas (Laird et al., 2009).

Depending on the thermal environment and the final temperature, pyrolysis will yield mainly biochar at low temperatures, less than 450 ^{0}C, when the heating rate is quite slow, and mainly gases at high temperatures, greater than 800 ^{0}C, with rapid heating rates. At an intermediate temperature and under relatively high heating rates, the main product is bio-oil.

2.10 FACTORS THAT AFFECT PYROLYSIS YIELD

The quality and distribution of pyrolysis products depend on the pyrolysis final temperature, heating rate, residence time, type of reactor, feedstock, etc (Zanzi, Sjostrom and Bjornbom, 1996).

2.10.1 Final temperature

In many pyrolysis studies, the increase of final temperature is always followed by an increase in the bio-oil yield, a decrease of bio-char yield and a slight increase in the gases amounts. In the pyrolysis of lard, Hassen-Trabelsi et al. (2013) showed that increasing the pyrolysis temperature

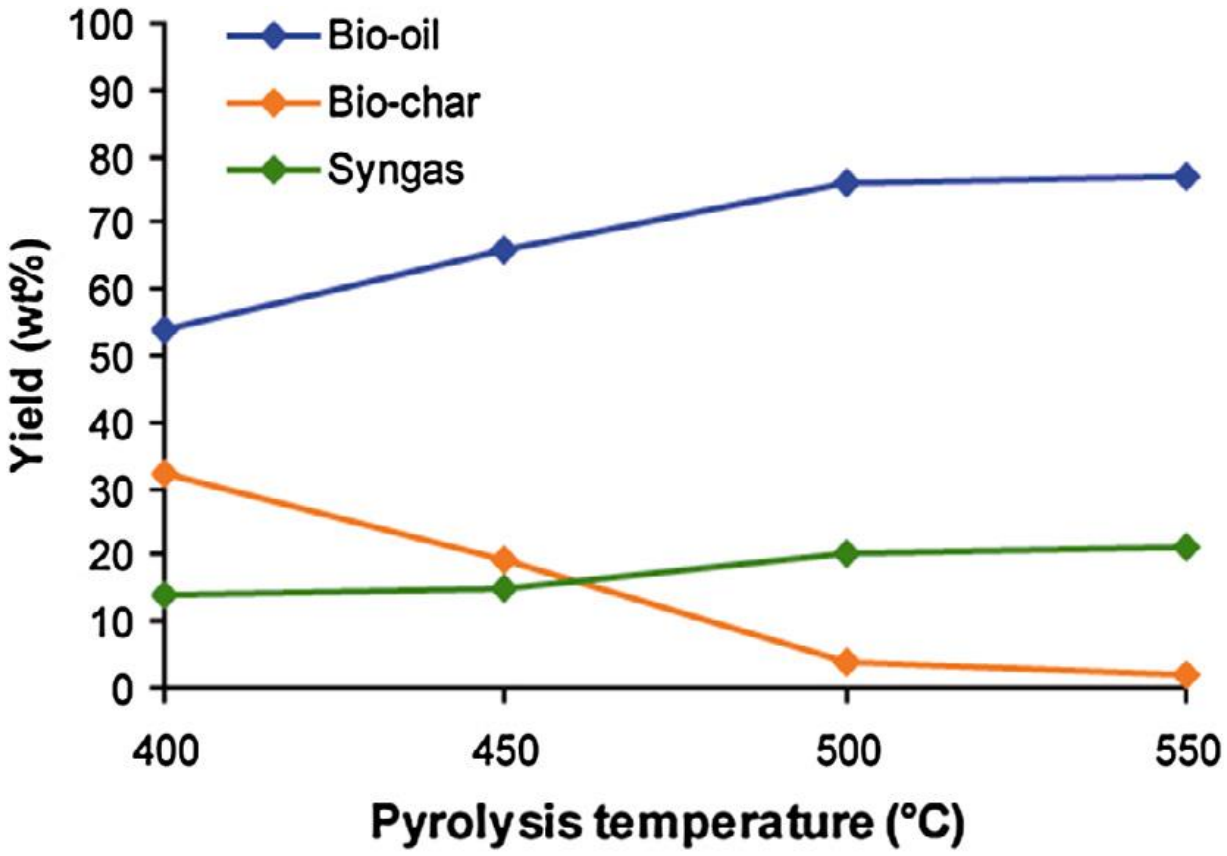


Figure 2.6 Effect of final temperature on pyrolysis products of lamb fatty wastes

(Hassen-Trabelsi et al., 2013)

from 400 °C led to a gradual increase in the fraction of bio-oil from 54 wt.% to 76 wt.% at 500 °C but there was no significant effect on the bio-oil yield when the temperature was raised from 500 °C to 550°C. The fraction of bio-char decreased from 32 wt.% and the gas fraction also showed an increase from 14 wt.% at 400 °C to 21 wt.% at 550 °C.

In the pyrolysis of bagasse, Asadullah et al. (2007) showed that increasing the pyrolysis temperature from 300 °C to 600 °C induced an increase in the bio-oil and gaseous products yields from 18.66 wt.% to 66.63 wt.% and from 4.34 wt.% to 14.71 wt.% respectively with a corresponding decrease of bio-char yield from 77 wt.% to 24.66 wt.%.

2.10.2 Heating rate

Different trends were reported by authors working with different type of wastes. Hassen-Trabelsi et al. (2013) showed that the effects of the heating rate on the pyrolysis products distribution of animal fat waste are almost the opposite of those observed for pyrolysis temperature. Increasing the heating rate from 5 °C /min to 15 °C /min significantly decreased the bio-oil yield from 80

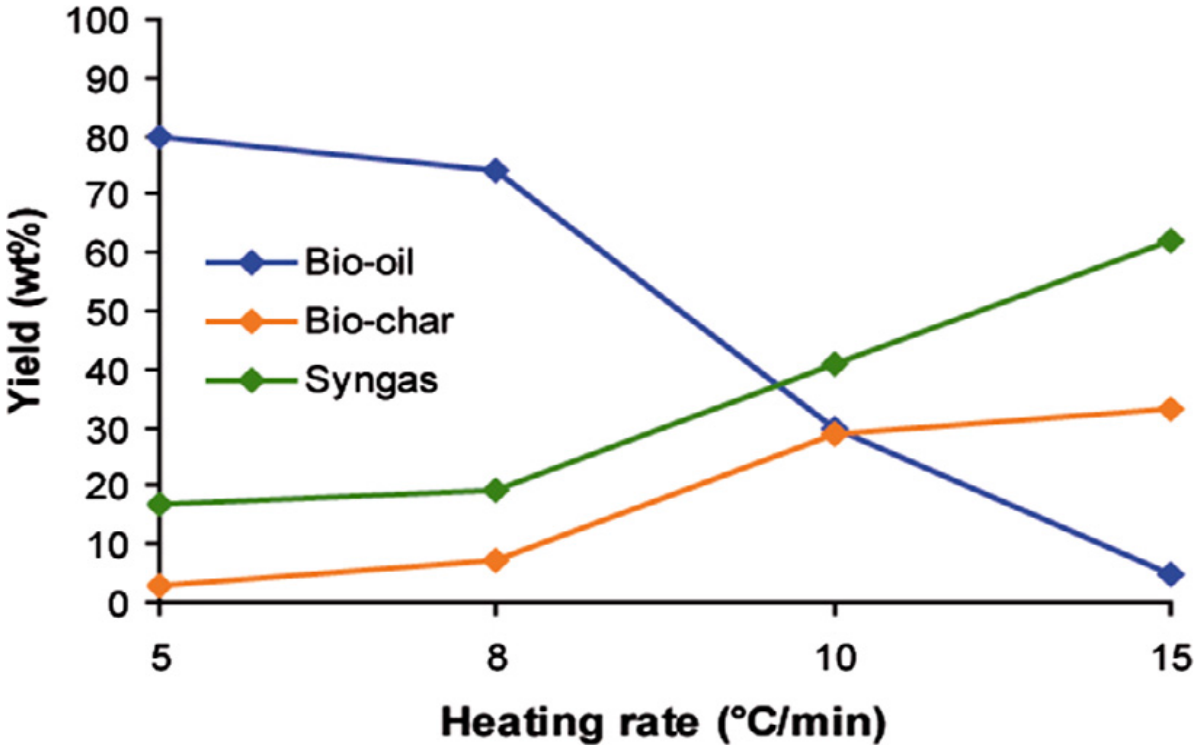


Figure 2.7 The effect of heating rate on pyrolysis products of lamb fatty wastes (Hassen-Trabelsi et al., 2013)

wt.% to 5 wt.% while the bio-char yield increased from 3 wt.% to 33 wt.% and the syngas proportion increased from 17 wt.% to 62 wt.%. They explain these behaviors to be the cracking of the liquid phase due to the increase of the heating rate. In fact, the long carbon chains contained in condensable vapors can be broken into short ones, inducing an increase in gaseous products (ibid).

2.10.3 Residence time

Adebanjo, Dalai and Bakhishi (2005) defines residence time as a ratio of packing volume and carrier gas volumetric flow rate at the reactor temperature. They showed that the volume of the product gas increased with increase in residence time (2.8 – 1.2 s) but the calorific values were high for all residence times. A maximum value of 133 MJ/m3 was obtained at residence time of 1.8 s. The yields of both the total and the diesel-like liquid decreased with increase in residence time.

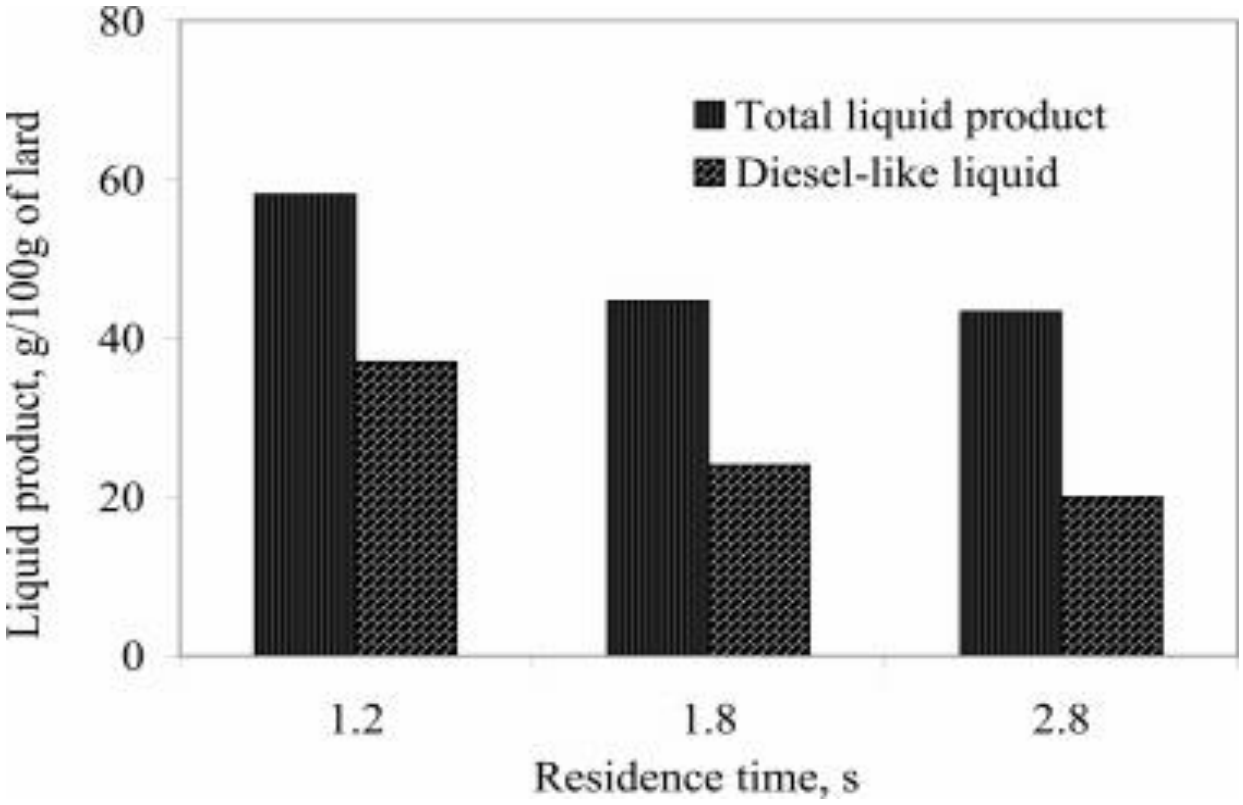


Figure 2.8 Effects of residence time on liquid yield of lard pyrolysis (Adebanjo, Dalai and Bakhishi, 2005)

Therefore, an increase in residence time (from 1.2 to 2.8 s) is detrimental to liquid production as well as the viscosity, which increased from 1.8 to 3.8 mPa. s as the residence time increased. The Cetane Index (CI) is maximized at a residence time of 1.8 s. This implies that too low residence time can also be detrimental to the quality of the liquid product.

2.10.4 Type of reactor

The reactor, of which they are various types, is at the heart of pyrolysis process. There have been considerable research, innovation and development to improve the essential characteristics. Initially, reactor developers had assumed that small biomass particles size and very short residence time would achieve high bio-oil yield. However, later research found that particle size and vapour residence time have little effect on bio-oil yield but influence bio-oil composition (Wang et al., 2005). With continuous reactor design development, a number have been developed to optimize the pyrolysis performance and to produce high quality bio-oil. However, each reactor type has specific characteristics, bio-oil yielding capacity, advantages and limitations. The different types of reactors are Fixed Bed, Fluidized Bed, Ablative, Vortex, Vacuum Pyrolysis, Rotating Cone, PyRos, Auger, Plasma, Microwave, Solar (Jahirul et al., 2012).

2.10.4.1 Fixed-Bed Reactor

This reactor consists of a gas cooling and cleaning facility. In the reactor, the solids move down a vertical shaft and contact a counter-current upward-moving product gas stream. Typically, this reactor is made of firebricks, steel or concrete with a fuel feeding, ash removal and gas exit units. They operate with high carbon conservation, long residence time, low gas velocity and low ash carry over (Altafini, Wander and Barreto, 2003). They are considered for small scale heat and power applications. The cooling system and gas cleaning consists of filtration through a cyclone, wet scrubbers and dry filters (Barker, 1996). The major problem of fixed bed reactors is tar removal; however recent progress in thermal and catalytic conversion of tar has offered options for removing tar (Rao et al., 2004)

2.10.4.2 Fluidized-Bed Reactor

Fluidized-bed reactors, as shown in Figure 2.9 consist of a fluid-solid mixture that exhibits fluid-like properties when pressurized fluid is introduced through the solid particulate substance. These reactors seem popular for fast pyrolysis as they provide rapid heat transfer, good control for pyrolysis reaction and vapour residence time, extensive high surface area contact between fluid and solid per unit bed volume, good thermal transport inside the system and high relative velocity between the fluid and solid phase (Lv et al., 2004). The different types of fluidized-bed reactors are Bubbling Fluidized-Bed and Circulating Fluidized-Bed, Rotating Disk, Reactors.

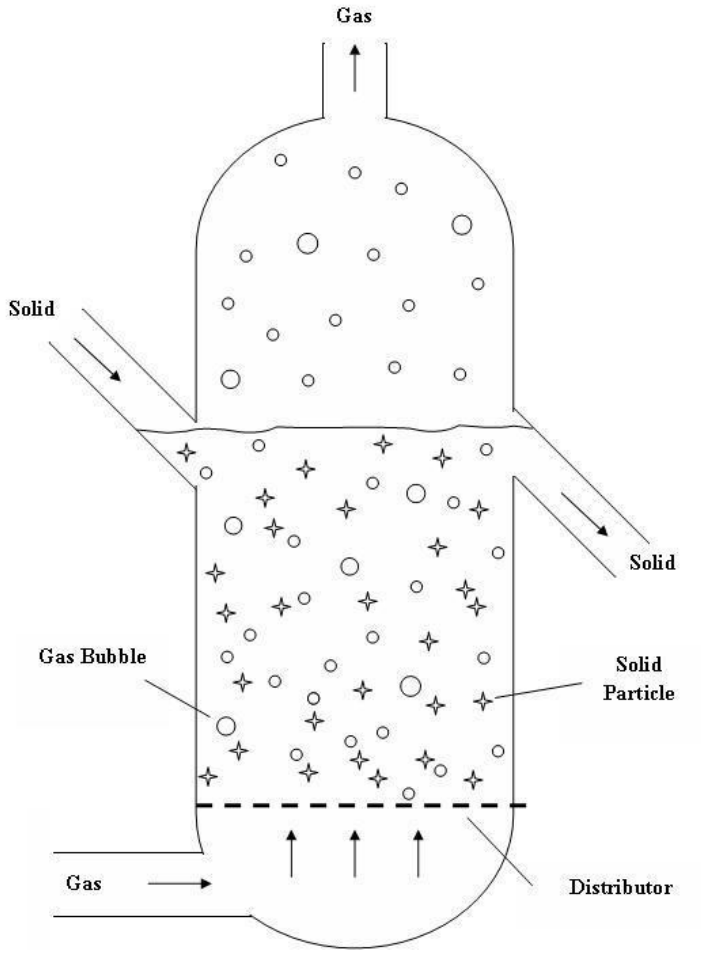


Figure 2.9 Fluidized Bed Reactor (Hughes, 2007)

2.10.4.3 Ablative Reactor

Ablative pyrolysis is fundamentally different from fluid bed processes in that heat transfer is through a molten layer at the hot reactor surface with the absence of a fluidizing gas. Mechanical pressure is used to press biomass against a heated reactor wall which then "melts" and, as it is moved away, the residual oil evaporates as pyrolysis vapours (Jones et al., 2009). Advantages of ablative reactors are that feed material does not require excessive grinding, and the process allows much larger biomass particle size than other types of pyrolysis reactors. This configuration is more complex due to the mechanical nature of the process. Scaling is a linear function of the heat transfer as this system is surface area controlled.

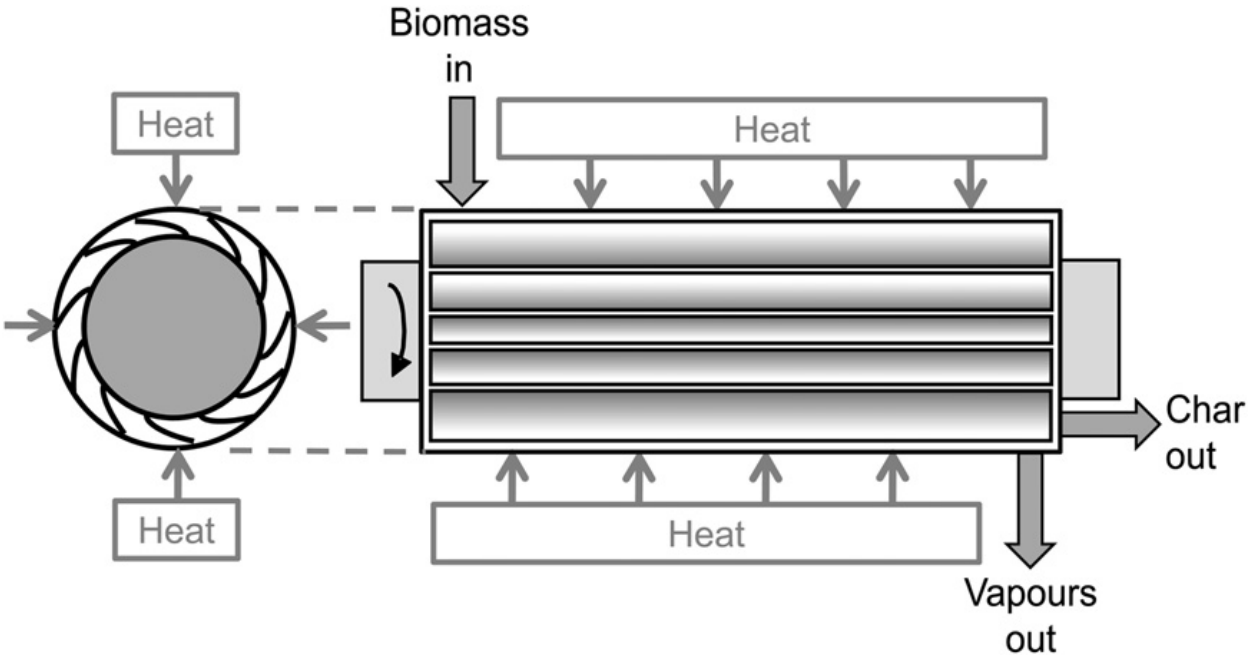


Figure 2.10 Ablative Reactor (Bridgwater, 2012)

2.10.5 Feedstock

Almost any form of organic material can be introduced into a pyrolyzer as the feedstock because the high temperature of the pyrolysis process neutralizes any organic toxins and pathogens in it. Chemical properties of the feedstock have a significant influence on both product yields and product quality (Laird et al., 2009). Among cellulosic feedstocks, bio-oil yield decreases with increasing ash content while the average molecular weight of the bio-oil fraction increases with lignin content of the feedstock (Fahmi et al., 2008).

In the pyrolysis of lamb, poultry and swine fats, Hassen-Trabelsi et al. (2013) showed that lamb fats produced the highest liquid yield of 77.9 wt.% while poultry and swine wastes produced 67.6 and 58.0 wt.%, respectively. The liquid condensate consisted of the aqueous (bottom phase) and organic-rich (upper phase). For the three studied samples, the organic-rich phase had the highest percentage of liquid fraction (between 45.8 and 61.6 wt.%) compared to the bottom one which presented small amounts (between 12.2 and 21.5 wt.%). Other authors who worked with similar type of triglycerides based wastes recorded higher yields of bio-oil. Demirbas (2007) reported a 77.1 wt.% of bio-oil for pyrolysis of beef tallow at 500 °C while Wiggers et al. (2009) obtained a yield of 73 wt.% for fish oil wastes at 525 °C and Wisniewski et al. (2010) reported a 72–73 wt.% from waste fish oil pyrolysis Wisniewski et al. (2010).

Mohan et al. (2006) concurs with Hassen-Trabelsi et al. (2013) that the increase of the heating rate induced an enhancement of bio-oil production in the pyrolysis of woody materials. However, Inguanzo et al. (2002), who studied the pyrolysis of sewage sludge established that the higher the pyrolysis heating rate, the more efficient the pyrolysis, i.e. a higher production of pyrolytic oil. This suggests that the pyrolytic behavior resulting from the heating rate variation can be linked to the raw feedstock composition: fatty materials differ from lignocellulosic biomass in their constitutional compounds (mainly fatty acids), high C, O, H and low ash contents (Hassen-Trabelsi et al., 2013). Thus, in the case of triglycerides materials, a high heating rate can induce a cracking of condensable vapors (Hassen-Trabelsi et al., 2013).

2.11 ADVANTAGES OF PYROLYSIS OVER TRANS-ESTERIFICATION

- Lower processing costs.
- Compatibility with infrastructure, engines and fuel standards.
- Feedstock flexibility.
- The final products are similar to diesel fuel in composition (Stumborg et al., 1996).

2.12 PRODUCTS OF PYROLYSIS

2.12.1 Bio-oil

The liquid product from biomass pyrolysis is known as biomass pyrolysis oil, bio-oil, or bio-crude. It is dark brown in colour. It is composed of a very complex mixture of oxygenated hydrocarbons with an appreciable proportion of water from both the original moisture and reaction product and can be used directly as a liquid fuel or as source of synthetic chemical feedstocks (Bridgwater, 2012). Solid char may also be present. It is unstable during pyrolysis but its chemical composition tends to change toward thermodynamic equilibrium during storage (Qi et al., 2006). The primary disadvantages of using the bio-oil as a diesel fuel include the low Higher Heating Value (HHV) which is approximately 40% less than that of fuel oil, high viscosity, and substantial solids content (Bridgwater, 2003). Additionally, the high water content that cannot be readily separated causes miscibility problems with conventional fuel oils, making blending impossible (Bridgwater, 2012).

Table 2.9 Typical properties of wood pyrolysis bio-oil and of heavy fuel oil (Mohan, Pittman, and Steele, 2006)

Physical property	**Bio-oil**	**Heavy fuel oil**
Moisture content (wt%)	15–30	0.1
pH	2.5	-
Specific gravity	1.2	0.94
Elemental composition (wt%)		
C	54–58	85
H	5.5–7.0	11
O	35–40	1.0
N	0–0.2	0.3
Ash	0–0.2	0.1
HHV (MJ/kg)	16–19	40
Viscosity (at 50 C) (cP)	40–100	180
Solids (wt%)	0.2–1	1
Distillation residue (wt%)	up to 50	1

Adebanjo et al. (2005) pyrolyzed lard in a continuous microreactor loaded with different sized quartz chips at atmospheric pressure and temperatures of 600°C and 800°C to produce a 37 wt.%

yield of liquid product of which a portion of its fraction resembled diesel fuel. Some of the components that determine the quality of bio-oil are:

2.12.1.1 Water

Bio-oil has water content of 15–30 wt% derived from the original feedstock moisture and the product of dehydration of the pyrolysis reaction and storage. The presence of water lowers the heating value and flame temperature, but on the other hand, it reduces the viscosity and enhances the fluidity, which is good for its atomization and combustion in the engine. Shihadeh and Hochgreb (2002) compared bio-oils from two sources and found that additional thermal cracking improved its chemical and vaporization characteristics. The better performance and ignition of one derived from its lower water content and lower molecular weight (Qi et al., 2006).

2.12.1.2 Oxygen

The structural oxygen content of a fuel improves its combustion efficiency due to an increase in the homogeneity of oxygen with the fuel during combustion. The oxygen in biodiesel improves the combustion process and decreases its oxidation potential. Thus, the combustion efficiency of biodiesel is higher than that of petrodiesel (Demirbas, 2009). But high oxygen content in the bio-oil leads to its poor stability and non-miscibility with hydrocarbons (Oasmaa and Peacocke, 2010). The oxygen content of bio-oils is usually 35–40% (Oasmaa and Czernik, 1999) distributed in more than 300 compounds depending on the feedstock and severity of the pyrolytic processes. Its presence creates the primary issue for the differences between bio-oils and hydrocarbon fuels. The high oxygen content lowers by 50%, the energy density in relation to the conventional fuel (Qi et al., 2006).

2.12.1.3 Viscosity

Depending on the feedstock and pyrolytic process, the viscosities of bio-oils vary widely. Those produced from Pterocarpus indicus and Fraxinus mandshurica by Luo et al. (2004) had a kinetic viscosity of 70–350 mPa s and 10–70 mPa s, respectively, while that from rice straw had 5–10 mPa s because of its high water content. Sipila et al. (1998) investigated the bio-oils from hardwood, softwood and straw by flash pyrolysis in an atmospheric fluidized bed and found that their viscosities were reduced in those with higher water content and less water insoluble

components. Viscosity was also affected by alcohols: a 5 wt% methanol introduced into hardwood pyrolysis oil with low methanol content decreased its viscosity by 35%. The straw oil is less viscous and had the highest methanol content of 4 wt%. Boucher et al. (2000) added methanol to bio-oil and this reduced its density and viscosity and increased its stability with the limitation of a lowered flash point. The flash point of a chemical is the lowest temperature where enough fluid can evaporate to form a combustible concentration of gas.

2.12.1.4 Acidity

Bio-oils comprise substantial amounts of carboxylic acids, such as acetic and formic acids, which leads to low pH values of 2–3. The bio-oil of pine had a pH of 2.6, while that of hardwood was 2.8 (Sipila et al., 1998). Acidity makes bio-oil extremely unstable, very corrosive and extremely severe at elevated temperature, which imposes more requirements on construction materials of the vessels and the upgrading process before using bio-oil in transport fuels (Bridgwater, 2012).

2.12.1.5 Heating value

Usually the bio-oils of oil plants have a higher heating value than those of straw, wood or agricultural residues. Beis, Onay and Kockar (2002) conducted pyrolysis experiments on safflower seed and obtained bio-oil with a heating value of 41.0 MJ/kg and a maximum yield of 44%. Ozcimen and Karaosmanoglu (2004) produced bio-oil from rapeseed cake in a fixed bed with a heating value of 36.4 MJ/kg and a yield of 59.7%. But bio-oils from wood and agricultural residues had a heating value of about 20 MJ/kg and a yield of up to 70–80%.

2.12.1.6 Ash

The presence of ash in bio-oil can cause erosion, corrosion and kicking problems in the engines and the valves, and even deterioration when the ash content is higher than 0.1 wt% (Qi et al., 2006). However, alkali metals are problematic components of the ash. More specifically, sodium, potassium and vanadium are responsible for high temperature corrosion and deposition, while calcium is responsible for hard deposits. The H50 bio-oil was found to contain 2 ppm K, 6 ppm Na and 13 ppm Ca (Boucher et al., 2000). The best job of hot gas filtering to date at NREL

resulted in <2 ppm alkali metals and 2 ppm alkaline earth metals in the bio-oil (Scahill, Diebold, and Feik, 1996).

Table 2.10 lists the cause and effects of the characteristic problems of pyrolized bio-oil.

Table 2.10 Characteristics of bio-oil (Bridgwater, 2012)

CHARACTERISTIC	CAUSE	EFFECTS
Acidity or Low pH	Organic acids from biopolymer degradation	Corrosion of vessels and pipework
Aging	Continuation of secondary reactions including polymerisation	Slow increase in viscosity from secondary reactions such as condensation Potential phase separation
Alkali metals	Nearly all alkali metals report to char; so not a big problem High ash feed, Incomplete solids separation	Catalyst poisoning Deposition of solids in combustion Erosion and corrosion Slag formation Damage to turbines
Char	Incomplete char separation in process	Aging of oil Sedimentation Filter blockage Catalyst blockage Engine injector blockage Alkali metal poisoning
Chlorine	Contaminants in biomass feed	Catalyst poisoning in upgrading
Colour	Cracking of biopolymers and char	Discolouration of some products such as resins
Contamination of feed	Poor harvesting practice	Contaminants notably soil act as catalysts and can increase particulate carry over.
Distillability is poor	Reactive mixture of degradation products	Bio-oil cannot be distilled - maximum 50% typically. Liquid begins to react at below 100 _C and substantially decomposes above 100 _C
High viscosity		Gives high pressure drop increasing equipment cost High pumping cost Poor atomisation

Low H:C ratio	Biomass has low H:C ratio	Upgrading to hydrocarbons is more difficult
Materials incompatibility	Phenolics and aromatics	Destruction of seals and gaskets
Miscibility with hydrocarbons is very low	Highly oxygenated nature of bio-oil	Will not mix with any hydrocarbons so integration into a refinery is more difficult
Nitrogen	Contaminants in biomass feed High nitrogen feed such as proteins in wastes	Unpleasant smell Catalyst poisoning in upgrading NOx in combustion
Oxygen content is very high	Biomass composition	Poor stability, Non-miscibility with hydrocarbons
Phase separation or In-homogeneity	High feed water, High ash in feed, Poor char separation,	Phase separation Partial phase separation, Layering; Poor mixing, Inconsistency in handling, storage and processing
Smell or odour	Aldehydes and other volatile organics, many from hemicellulose	While not toxic, the smell is often objectionable
Solids	See also Char Particulates from reactor such as sand Particulates from feed contamination	Sedimentation Erosion and corrosion Blockage
Structure	The unique structure is caused by the rapid de-polymerisation and rapid quenching of the vapours and aerosols	Susceptibility to aging such as viscosity increase and phase separation
Sulphur	Contaminants in biomass feed	Catalyst poisoning in upgrading
Temperature sensitivity	Incomplete reactions	Irreversible decomposition of liquid into two phases above 100 _C Irreversible viscosity increase above 60 _C Potential phase separation above 60 _C
Toxicity	Biopolymer degradation	Human toxicity is positive but small

	products	Eco-toxicity is negligible
Viscosity	Chemical composition of bio-oil.	Fairly high and variable with time Greater temperature influence than hydrocarbons
Water content	Pyrolysis reactions, Feed water	Complex effect on viscosity and stability: Increased water lowers heating value, density, stability, and increase pH Affects catalysts

2.13 BIO-CHAR

The byproduct char is typically about 15 wt.% of the products but about 25% of the energy of the biomass feed (Bridgwater, 2011). The low thermal conductivity of biomass gives low heating rates through larger particles which leads to increased char formation and hot char is known to be catalytically active. It cracks organic vapours to secondary char, water and gas both during primary vapour formation and in the reactor gas environment. Therefore, its rapid removal from the hot reactor environment and minimal contact with the pyrolysis vapour products is essential (Bridgwater et al., 1999). As particle size increases, liquid yields reduce as secondary reactions within the particle become increasingly significant (Scott and Piskorz, 1984).

The char can be used to provide the process heat requirements by combustion or it can be separated and exported, in which case an alternative fuel is required. The fresh char is pyrophoric i.e. it spontaneously combusts when exposed to air so careful handling and storage is required. This property deteriorates with time due to oxidation of active sites on the char surface (Bridgwater, 2011).

Low-ash bio-chars are used in metallurgy and as a feedstock for production of activated carbon, which is used as an adsorbent to remove odorants from air streams, and both organic and inorganic contaminants from waste-water streams (Laird et al., 2009). An emerging new use of biochar is as a soil amendment (Laird et al., 2009).

2.14 BIO-GAS

Biogas (syngas) in pyrolysis is the incondensable gases emanating from the process while the condensable gases form the bio-oil. Syngas is primarily a mixture of H_2 and CO, but often contains CH_4, CO_2, H_2O, and several low molecular-weight volatile organic compounds (Ioannidou et al., 2009). The heating value of syngas is relatively low (~6 MJ kg-1) compared to that of natural gas (~54 MJ kg-1) (Laird 2009). This syngas could be used to generate the heat and electricity needed to run the pyrolyzer.

2.15 CATALYSIS IN THE PYROLYSIS OF FATS

Catalysis plays a central role in chemical transformations and lies at the heart of countless chemical protocols (Hemalatha et al., 2013). Through catalysis, one can reduce the temperature of a reaction, reduce waste and enhance selectivity of a desired reaction. In the absence of a catalyst, variety of products would not be feasible. Among the three well-known catalysis categories - homogeneous, heterogeneous and enzymatic catalysis, enzymatic catalysis is the most efficient and greenest. The homogeneous and heterogeneous catalysis have their own merits and demerits hence there is urgent need for a new catalytic system, which should embrace all the merits of both catalysis (Gawande et al., 2013).

Product selectivity and yield determines the catalyst to be used. The two major groups of catalysts used are transition metal catalysts and molecular sieve type catalysts. When transition metal catalysts are used under high hydrogen partial pressures, the result is diesel-like products while molecular sieve catalysts result in highly aromatic, gasoline type products. Pure insulator oxides, most notably activated alumina, and sodium carbonate represent the two other groups of catalysts.

2.15.1 Transition Metal Catalysts

Many researchers have used the transition metal catalysts to produce diesel like hydrocarbons from triglycerides (Maher et al., 2007). da Rocha Filho et al. (1993) investigated the formation of alkanes, alkylcycloalkanes and alkylbenzenes during the catalytic hydrocracking of vegetable oils using a $NiMo/Al_2O_3$ catalyst in the presence of elemental sulfur at temperatures ranging from 350–450 °C and pressures between 7–14 MPa. The primary reaction products consisted primarily of C11–C18 alkanes (65.3–76.8 wt.% of feed).

In a similar study, da Rocha Filho et al. (1992) cracked seringa and ucuuba oils using the same catalyst at 360 °C and 14 MPa. Conversions of almost 100% were obtained and the primary products were found to be alkanes and cycloalkanes. The gas phase, aromatics, and acid values were not as significant.

Craig and Coxworth (1987) used a conventional fluid catalytic cracking (FCC) bench scale unit and hydrocracking/hydrotreating techniques to convert canola oil into hydrocarbons with yields similar to conventional petroleum based feedstocks in the FCC unit. Subsequent hydrotreating yielded fuels in the diesel boiling range. The success of these studies has led to the commercialization of a ‘‘super cetane’’ product to be used as a diesel fuel additive. This technology utilizes conventional refining technology with different fatty feeds. The product is separated into three fractions: naptha, middle distillates, and waxy residues. The middle distillate or super cetane, composed primarily of straight chain hydrocarbons, has similar characteristics to diesel fuel and a cetane number of approximately 100 (CANMET Energy Technology Center, 2004).

2.15.2 Molecular Sieve Catalysts

Molecular sieve catalysts are highly crystalline and porous whose activity and selectivity depend on factors such as acidity, pore size and distribution, and pore shape (Twaiq et al., 1999). Through size selectivity, they allow only molecules of a certain size to pass through, hence the pore size can be altered to obtain specific reaction products (Maher et al., 2007).

Zeolite is the broad term used to describe a family of minerals called tectosilicates. These minerals contain small pores which provide a generous surface area. Currently, there are 40 known natural zeolites and in excess of 140 synthetic zeolites (Marcus and Cormier, 1999). Zeolite catalysts are crystalline alumino-silicate materials based on a three dimensional network of AlO_4 and SiO_4 tetrahedrally linked through oxygen atoms which offer significant advantages over amorphous silica–alumina catalysts (Campbell, 1983).

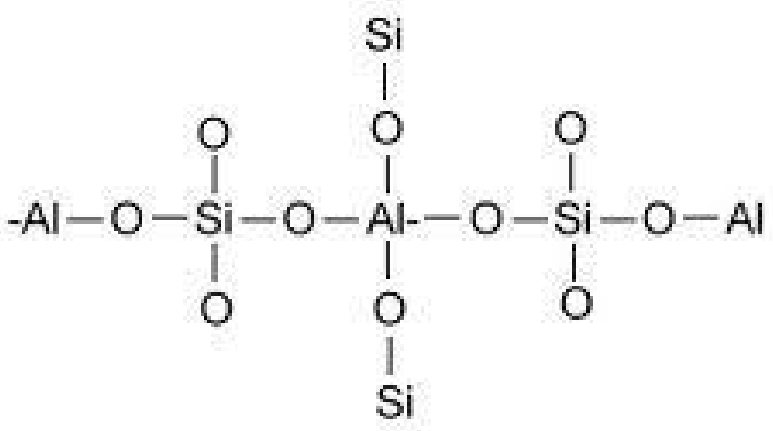


Figure 2.11 Basic Zeolite structure (www.cheresources.com/zeolitezz.shtml)

A high-silica zeolite catalyst, HZSM-5, has the ability to convert a huge range of materials to high-octane, aromatic, gasoline like products (Milne et al., 1990). Katikaneni et al., (1995a,b,c) has shown that the HZSM-5 catalyst was the most effective type of zeolite catalyst for converting vegetable oil to gasoline range hydrocarbons but according to Twaiq et al. (1999), they still exhibit high gas formation, which will decrease the formation of the desired liquid fraction.

A mesoporous catalysts, MCM-41 which has shown selectivity for C5 olefinic products was used to study the effect of the percentage of alumina incorporated into a catalyst on the product distribution of cracked palm oil by Twaiq et al. (2003). They found that an increase in alumina increased catalyst acidity and activity to an optimum level. This resulted in lower gas formation but they were more selective for linear hydrocarbons in the diesel boiling range rather than gasoline range. However, the activity was lower than the HZSM-5 catalyst.

Sang et al. (2003) compared the performance of HSZM-5, MCM-41 and their composite catalysts. The composite catalyst resulted in the highest conversion (99 wt.%) and highest gasoline yield. They found that reaction temperature, catalyst ratio, and WHSV (Weight Hourly Space Velocity) were the important operating variables in terms of the final product distribution. The optimum yield of gasoline was found at a reaction temperature of 440 °C, fatty acid to catalyst ratio of 9.64, and WHSV of 3.66 h^{-1}. According to Putin and Putun, (2009), biomass-derived oils are generally best upgraded by HZSM-5 or ZSM-5, as these they promote high yields of liquid products and propylene.

The motivations for using zeolite nano-catalysts are basically for cost effectiveness and environmental regulation compliance. Zeolites can help yield products at milder temperatures and pressures which lowers operating costs. They also have superior control of reaction selectivity which saves on feed costs and by reducing waste streams saves on treatment costs (Marcus and Cormier, 1999). Unfortunately, they tend to coke easily, and give high TANs (Total Acid Number) and undesirable byproducts such as water and CO_2.

- Advantages of Zeolite as a Catalyst

a. Reduction of NOx emission by selective catalytic reduction (SCR).
b. Direct oxidation of benzene to phenol which eliminates cumene as an intermediate and uses nitrous oxide (N_2O) as a reactant. Nitrous oxide is a typical waste stream from adipic acid production.
c. Conversion of ethylbenzene to styrene at moderate temperatures and pressures. This process eliminates xylene as a by-product and which further eliminates several purification steps.
d. Caprolactam via oxidation which drastically reduces the number of processing steps as well as waste streams.
e. It has the ability to regenerate/recycle a process' catalyst. Many catalysts must be disposed of after they are spent, but the impregnating of zeolites is a process that can be repeated over and over. Ironically, zeolites themselves help reduce waste. (Marcus & Cormier, 1999).

2.15.3 Activated Alumina

It has been shown that activated alumina is an effective catalyst for decarboxylation of fatty acids at atmospheric pressure and 450 °C (Vonghia et al., 1995). Pure insulator oxides including MgO, SiO_2 and Al_2O_3 are important catalysts that are not notably acidic, and their main activity is dehydration (Campbell, 1983). Konar et al. (1994) pyrolysed trinolein, canola oil, trilaurin and coconut oil over activated alumina at 450 °C under atmospheric pressure and the liquid yields of 65–79% were hydrocarbon mixtures containing n-alkanes and n-alkenes with a marked absence of oxygen. Dos Anjos et al. (1983) pyrolyzed crude and hydrogenated soya oil over MgO and alumina at temperatures of 300–350 °C and the result was only a partial conversion to hydrocarbons. The products contained approximately 50% carboxylic acids and 25– 28% hydrocarbons.

2.15.4 Sodium Carbonate

Dandik and Aksoy, (1998b), Konwer et al. (1989), and Zaher and Taman, (1993) have all used sodium carbonate catalyst in the pyrolysis of vegetable oils. Konwer et al. (1989) catalysed the production of liquid fuel from Mesua ferrea L. seed oil and the pure forms of its primary fatty acids including linolinic, linoleic, oleic, palmitic, and stearic acid with solid sodium carbonate. They catalyzed this oil with 1% sodium carbonate at 500 °C to produce black pyrolytic oil whose fractions are suitable for various applications including gasoline and diesel.

Dandik and Aksoy (1998b) used sodium carbonate in the pyrolysis of used sunflower oil in a reactor equipped with a fractionating packed column but contrary to the results of Konwer et al. (1989) their study showed very low conversions and concentrations of aromatics in the pyrolysis products and almost half of the feed formed coke-residual oil. The primary pyrolysis products consisted of liquid and gaseous hydrocarbons phases with lesser amounts of acids, water, H_2, CO, and CO_2. The liquid phase contained mostly C_5–C_{11} hydrocarbons (19.45–32.87%) and the gaseous phase was mainly composed of C_1–C_3 hydrocarbons (13.65–26.18%).

Zaher and Taman (1993) pyrolyzed cottonseed oil in the presence of 1% sodium carbonate. The product, approximately 70 wt.% of the original oil comprised of nearly 70% Alkanes and 21.7% aromatics. Dandik and Aksoy (1999) compared the pyrolysis of used sunflower oil using sodium carbonate, silica–alumina, and HZSM-5 catalysts and obtained the highest conversion (73.17 wt.%) with sodium carbonate as catalyst, resulting in the highest yield of liquid product primarily consisting of gasoline range hydrocarbons. A possible concern with sodium carbonate is that traces of sodium may be present in the product, impeding its use, though, there were no reports of such. It is however, likely that the sodium carbonate first reacts with fatty acids to produce sodium salts which are then further decomposed into hydrocarbons (Konwer et al., 1989).

2.16 NANO-CATALYSIS

Nanoparticles (NPs) are particles sized between 1-100 nano-meters (10^{-9} meters). Synthesis of stabilized nanoparticles sized between 1-100 nm is the main task of the nanochemistry. As restriction arises from its definition, the chemistry of nanoparticles depends mainly on two things - synthesis of NPs well controlled in size and shape, and molecular approach to find more selective applications of NPs especially in nanocatalysis.

Nano-catalysts have combined advantages of both the homogeneous and heterogeneous catalytic systems. Nano-catalytic system allows the rapid, selective chemical transformations with excellent product yield coupled with the ease of catalyst separation and recovery. Recovery of catalysts from the system is the most important characteristic of any catalyst in industry. Because of nano size (high surface area) the contact between reactants and catalyst increases dramatically creating a pseudo-homogeneous phase. Insolubility in the reaction solvent makes the catalyst heterogeneous and hence can be separated out easily from the reaction mixture (Luo et al., 2012).

Table 2.11 Comparative efficiency of homogeneous, heterogeneous and nanocatalysis (Singh and Tandon, 2014)

<table>
<tr><th>Homogeneous Catalysis</th><th>Nano-Catalysis</th><th>Heterogeneous Catalysis</th></tr>
<tr><td>High activity</td><td rowspan="4">High activity
High selectivity
Excellent stability
Easily separable
Energy efficiency
Atom economy</td><td>Excellent stability</td></tr>
<tr><td>High chemo-and region-selectivity</td><td>Easy accessibility</td></tr>
<tr><td></td><td>Easily separable</td></tr>
<tr><td><u>Demerits</u>
Cumbersome product purification and difficulty in catalyst recovery</td><td><u>Demerits</u>
1. Inferior catalystic activity relative to their counterpart
2. Homogeneous and requires more reaction time</td></tr>
</table>

Recovery and recyclability of catalysts is an important factor in catalysis (Astruc et al., 2005). Recyclability of catalyst behaves like the bottleneck for industrial application of NPs in the solution phase. For this purpose, the deposition of pre-formed NPs onto supports to get heterogeneous systems easy to recover is being explored. But the use of magnetic supports to recover a catalyst from the catalytic media by simply applying a magnet appeared recently.

2.17 BENEFITS OF NANO-CATALYSIS

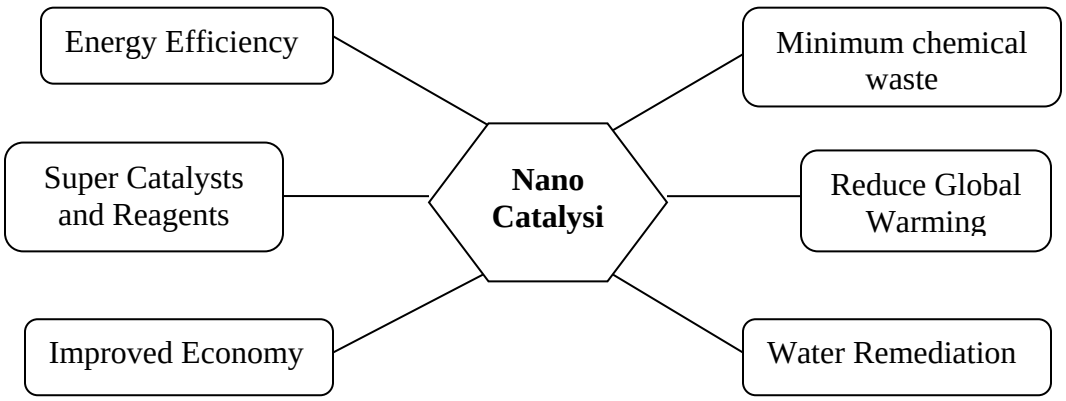


Figure 2.12 The benefits of nano-catalysis (Singh and Tandon, 2014)

2.18 SODIUM SILICATE AS A NANO-CATALYST IN THE PYROLYSIS OF FAT

According to Guo et al. (2010), inorganic solid bases, such as sodium silicate are low-cost and easy-to-use heterogeneous catalysts. They are used to catalyze the transesterification reaction for soybean oil to biodiesel with a yield of almost 100% with a sodium silicate of 3.0 wt %, a molar ratio of methanol/oil of 7.5:1, reaction time of 60 min, reaction temperature of 60 ºC, and stirring rate of 250 rpm.

In addition to high catalyst activity, sodium silicate also has other similar characteristics to supported-solid base catalysts. Most of its basic sites are in the interior of the solid catalyst due to low surface area and high density. A nano-sized sodium silicate catalyst will increase its surface area, exposing the highly reactionary sites, thus enhancing its catalyzing properties. The calcined sodium silicate could tolerate 4.0 wt% water or 2.5 wt% FFAs contained in soybean oil. This water tolerance is related to its special crystal and porous structure.

Long et al. (2011) used sodium silicate as catalyst for transesterification of rapeseed oil for several recycles, and subsequently the used sodium silicate without any modification was catalyzed for the hydrothermal production of lactic acid from glycerol at 300 °C. A yield of 80.5% lactic acid and only minor amounts of formic, acetic acid and acrylic acid were produced.

CHAPTER 3: MATERIALS AND METHODS

3.1 MATERIALS

The feedstock used in this study, waste cow fat (tallow), was obtained from Karan Beef (Pty) Ltd in City Deep, Johannesburg, South Africa. It was preserved in a freezer at -10 ^{o}C throughout the period of the experiments.

The commercially available zeolite powder (Product Number: 96096) manufactured by Sigma and of composition, 0.6 K_2O : 4.0 Na_2O : 1 Al_2O_3 : 2.0 " 0.1 SiO_2 : x H_2O and Particle Size <10μm was selected as the catalyst for the catalytic pyrolysis of the feedstock in the second part of the experiments.

3.2 TESTS TO CHARACTERIZE RAW MATERIALS AND PRODUCTS

3.2.1 CHNS-O Elemental Content

Prior to the pyrolysis experiments, the waste fats were freeze-dried and analyzed using elemental analysis (CHNS-O). The CHN-content of the input materials were determined by Flash 2000 CHNS-O analyzer fitted with an auto sampler (produced by Thermo Scientific).

A sample with a mass between 1.5 - 2.0 mg is weighed into a tin capsule and the capsule is folded and re-weighed. The sample is then placed into an auto sampler of the Flash 2000 CHNS-O and the instrument is set according to the following parameters:

He pressure	:	250 kPa
O_2 pressure	:	250 kPa
Furnace temperature	:	950 °C
Carrier flow	:	140 ml/min
Reference flow	:	100 ml/min
Oxygen flow	:	250 ml/min
Column oven temperature	:	65 °C
Sample holder	:	tin capsules.

For the determination of CHNS-O, the sample is introduced into a quartz reactor filled with electrolytic copper. The oxygen causes the combustion of the sample and the carrier gas (Helium) carries the sample through the reactor to the thermal conductivity detector (TCD) which is housed in an oven kept at 65 °C. The results are then processed and displayed onto the PC. Before the analysis can be conducted, a bypass sample, blank and calibration standards (BBOT, CYSTINE, METHIONINE AND SULFANIMIDE) are analyzed. The Oxygen determination is performed with the TCD detector polarity reversed. The oxygen content was calculated by difference.

3.2.2 Acid Value

702 SM Titrino was used to determine the acid value of the samples. 5 g of the sample was put into a 250 ml beaker and 30 ml of a mixed solvent of toluene, water and propanol was added. The ratio of the added mixture - toluene: water: propanol was 500:5:495. The content of the beaker was then titrated with 0.1 mol/l KOH to determine the acid number.

3.2.3 Ash Content

1 g of the sample was weighed into a porcelain crucible and then transferred into a muffle furnace which was set at 850° C. The sample was left overnight in the oven until the ashing process was complete. This was evident when the sample turned white. The % ash was then calculated after the sample was cooled and re-weighed.

3.2.4 pH

The Orion pH meter was calibrated using buffer solutions (pH 4, 7 and 9) and the sample then stirred into a slurry. The pH electrode was then inserted into a beaker containing the slurried sample and the reading obtained.

3.2.5 Density

The sample was stirred into a slurry and poured into a measuring cylinder which was placed over an analytical balance and weighed. Using the volume measured into the measuring cylinder, the density was the determined.

3.2.6 Calorific Value

A bomb calorimeter was used for the determination. The sample was weighed and transferred into a calorie meter cup, and the ignition wire was mounted. The bomb was tightly closed and then put under pressure with a gas. The bomb was placed into the calorimeter device were the ignition took place and the CV value was displayed on the device.

3.2.7 Mass Spectrometry-Gas Chromatography (GC–MS)

GC–MS analyses of the neutral fraction from bio-oils were performed using an Pegasus 4D GC x GC-MS TOF Low Resolution gas chromatograph. The injector was set at 250 ^{o}C and helium was the carrier gas. The GC oven was held at 40 ^{o}C for 2 min then heated to 300 ^{o}C at a rate of 5 _C min_1 and finally 30 min hold at 300 _C. The identification of the compounds was accomplished by advising a NIST database and comparing with published mass spectra.

3.2.8 Viscosity

This was performed by an Ubbelohde- viscosity meter. The sample is agitated into a viscous slurry and introduced into a capillary tube in order to determine its flow by using an equation by Poiseuille.

3.2.9 X-Ray Diffraction

The sample is dried in a conventional oven at 110 °C then it is milled until it is a fine powder. The milled sample is then mounted onto a sample holder which is then introduced into the XRD machine were measurement is then performed.

3.3 METHODS

3.3.1 PYROLYSIS EXPERIMENTAL SET UP AND PROCEDURE

The pyrolysis experiments were carried out in an Elite Pyrolysis Reactor Model - a laboratory scale fixed bed reactor heated by an electric furnace that was controlled by a PID Controller. The programming instruction of this PID Controller is in Appendix II. The reactor was made of stainless steel but protected with a plastic mesh that covered the whole circumference. The silica cylindrical tube inside which the pyrolysis takes place has the



Figure 3.1 The ELITE Reactor and Temperature Controller (PID)

following dimensions: height – 100cm; external diameter - 60 cm; mass - 822 g; volume – 2200 cm^3. The control board was adjusted to the desired temperature and heating rate for each experimental run according to Table 3.1.

Table 3.1: Control parameters for the pyrolysis experiments without a catalyst

Sample	**Final Temp** (^{o}C)	**Heating Rate** (^{o}C/min)	**Mass of Fat** (g)
B1	450	4	50
B2	450	5	50
B5	500	5	50
B6	500	6	50
B7	530	4	50
B8	530	5	50
B9	530	6	50
B10	580	4	50
B11	580	5	50
B12	580	6	50



Figure 3.2 Fat samples in silica boats about to be placed inside the reactor (Picture taken by author in Wits, 2015)

The silica tube containing the fat samples which were placed inside the reactor and during experiments had a height of 100cm, and internal diameter, 60cm. The extended ends of the silica tube kept the entry point of the Nitrogen carrier gas and the exit pyrolysis vapour from the furnace. The temperature was controlled by a thermocouple immersed inside the reactor. All pyrolysis experiments were carried out under atmospheric pressure and inert conditions. During experiments, the reactor was continuously flushed with nitrogen gas maintained at 50cm^3/min in order to remove air from the reactor and all the gases produced during pyrolysis. The joints were sealed with Parafilm and Gel to prohibit any form of leakage.

In all experiments, approximately 50 g of tallow of particle sizes between 0.6-0.85 mm were placed in silica boats inside the reactor, and were heated from room temperature until the desired temperature, and at different heating rates. They were held at the final temperature for 15 minutes until no further significant release of gas was observed.



Figure 3.3 The pyrolysis experiment in progress (Picture taken by author in Wits, 2015)

Gas and vapors formed during pyrolysis, flow out from the top of the reactor, and passed through a trapping system that consisted of a condenser cooled by cold water from a tap. The round-bottomed flask that trapped the condensed vapour product from the condenser, which is the bio-oil, is kept inside a container and the temperature maintained at 0 ^{o}C. The bio-oil consisted of two phases - an aqueous (bottom phase) and organic rich compounds (upper phase) that were separated by decantation. The yield of collected bio-oil was calculated by,

$$\frac{\text{mass of bio-oil collected}}{\text{total amount of initial feedstock}} \text{ X } 100$$

The residual bio-char was collected after completing the pyrolysis reaction and when the reactor was at room temperature. The bio-char yield was calculated by

$$\frac{\text{mass of bio-char collected}}{\text{total amount of initial feedstock}} \text{ X } 100$$

The non-condensable vapors passed through an exit line. The amount of non-condensable gases produced was determined by difference from mass balance.



Figure 3.4 The zeolite powder used in the pyrolysis and its container. (Picture taken by author in Wits, 2015)

CHAPTER 4: RESULTS AND DISCUSSION

4.1 RESULTS AND DISCUSSION

4.1.1 PROPERTIES OF THE BEEF FAT (TALLOW) USED IN THE PYROLYSIS

The physical properties of the tallow used in the pyrolysis experiments are given in Table 4.1.

Table 4.1 Properties of the tallow feedstock

Properties	Values
pH	5.72
Acid Value	225.32
% Ash	6.33
% C	76.06
% H	11.72
% O	12.21
% N	-
% S	0
Density (g/cm^3)	0.63
Calorific Value (MJ/kg)	39.41

The Calorific Value (CV) of the raw waste animal fat, 39.41 MJ/kg is within expected values but its density, 0.63 g/ cm^3 is slightly low. It is expected to increase in the product after pyrolysis due to the dehydrating nature of the process.

The trace amount of sulfur in the table, important criteria for its application as fuel, infers that the combustion product would contain trace amounts of the SO*x* pollutants.

The absence of nitrogen in the fat would have implied that there wouldn't be any of the nitrogen oxides (NO*x*) pollutants on combustion but because nitrogen was used as the carrier gas, the NO*x* pollutants would be formed on combustion at high temperature. The atmospheric nitrogen (N_2) entering the combustion zone as part of the combustion air also increases the nitrogen content of the fuel though not all of the fuel nitrogen is released during combustion.

It has high carbon and low oxygen contents. Its high ash content (6.33%) is cause for concern with regards to the aging and sedimentation of the produced oil, and which will cause filter blockage, engine injector blockage, etc.

The pH value is almost neutral, hence acceptable but when we consider the dehydrating nature of pyrolysis, it will be expected to reduce towards acidic values.

Table 4.2 Molecular composition of the fat feedstock

Organic Acid	Content (%)
Linoleic acid	1.69
Linolenic acid	1.05
Myristic acid	1.01
Oleic acid	52.82
Palmitic acid	17.73
Stearic acid	11.58
Others	14.12

4.2 PYROLYSIS EXPERIMENTS WITHOUT A CATALYST

Table 4.3 shows the result of the pyrolysis experiments performed by alternating the heating rates and the temperatures without a catalyst.

Table 4.3 The result of the pyrolysis experiments done without a catalyst

Sample	FT	HR	Vol of Biofuel produced	Mass of Biofuel produced	Mass of Char Produced	Mass of Incondensable gases	Yield of Biochar	Yield of Bio-oil wrt mass
	^{o}C	^{o}C/min	ml	g	g	g	%	%
B1	450	4	36.00	19.16	27.18	3.66	54.36	38.32
B2	450	5	35.00	18.43	15.00	16.57	30.00	36.86
B5	500	5	41.67	26.81	6.50	16.69	13.00	53.62
B6	500	6	44.80	28.28	9.85	11.87	19.70	56.56
B7	530	4	36.00	29.72	8.00	12.28	16.00	59.44
B8	530	5	37.00	31.00	8.32	10.68	16.64	62.00
B9	530	6	53.29	41.39	8.00	0.61	16.00	82.78
B10	580	4	40.00	33.30	4.00	12.70	8.00	66.60
B11	580	5	45.00	36.45	3.00	10.55	6.00	72.90
B12	580	6	39.00	33.00	8.00	9.00	16.00	66.00

4.2.1 Effect of Temperature on Yield

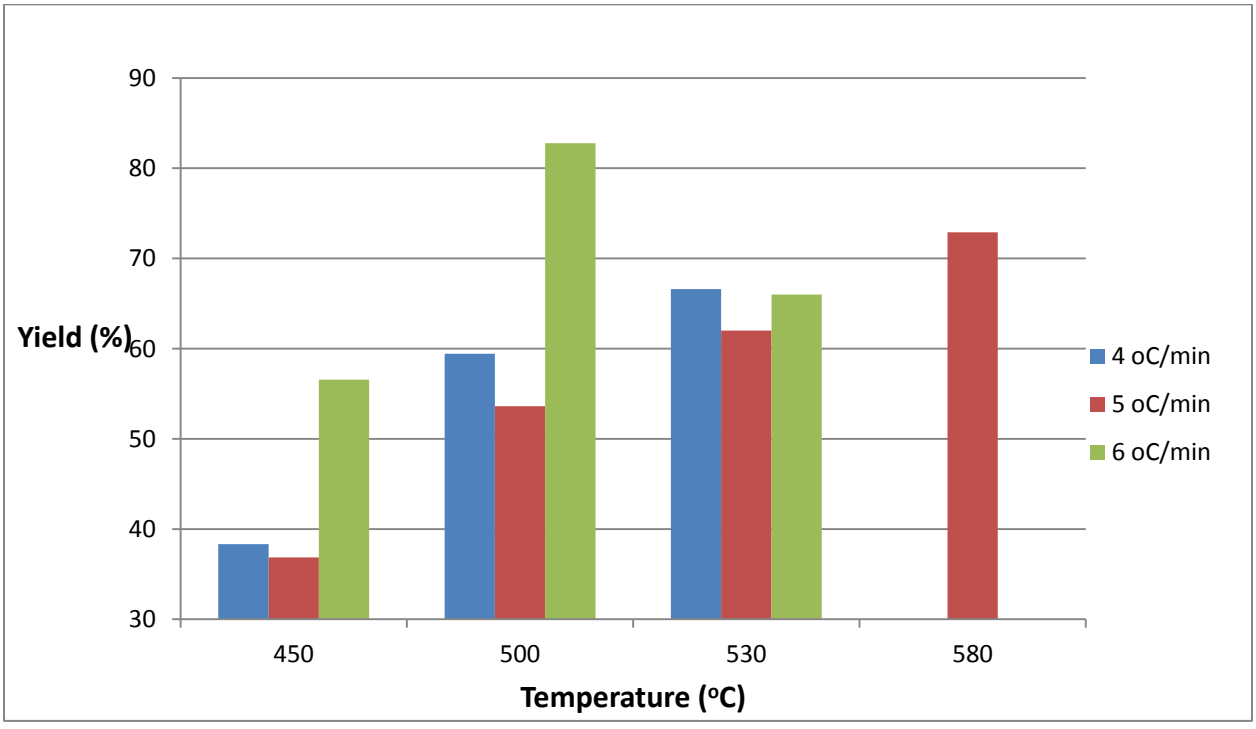


Figure 4.1 Yield of bio-oil using 4, 5 and 6^{o}C /min heating rates.

At the heating rate of 6^{o}C /min, as shown in **Figure 4.1**, there was an increase in the bio-oil yield from 56.56 % to 82.78 % when the final temperature was raised from 500^{o}C to 530^{o}C but declined to 66 % when the temperature was increased further to 580 ^{o}C. The 82.78 % yield from final temperature of 530^{o}C and heating rate of 6^{o}C /min happens to be the highest yield obtained for all the pyrolysis experiments conducted. The bio-oil yield at 5 ^{o}C /min heating rate and final temperatures of 450^{o}C, 500 ^{o}C, 530 ^{o}C and 580 ^{o}C are 36.86 %, 53.62 %, 62 % and 72.90% respectively, showing a markedly progressive trend.

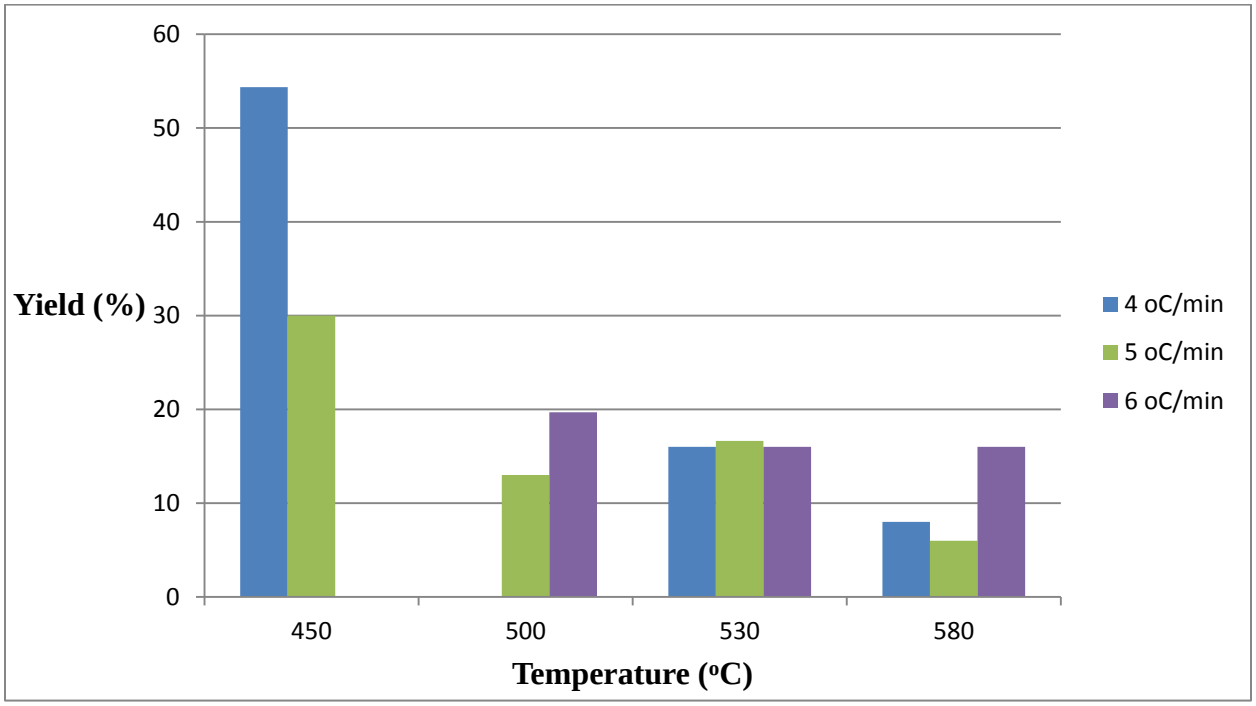


Figure 4.2 Yield of bio-char using 4, 5 and 6 ^{o}C /min heating rates.

As expected, the yield of the biochar **(Figure 4.2)** gradually declined; 30 %, 13 %, 16.64 % and 6% at final temperatures of 450^{o}C, 500 ^{o}C, 530 ^{o}C and 580 ^{o}C, respectively. Likewise, the incondensable gases mass declined **(Figure 4.3),** resulting in yields of 33.14 %, 33.38 %, 21.36 % and 21.1 % at the final temperatures of 450^{o}C, 500 ^{o}C, 530 ^{o}C and 580 ^{o}C, respectively.

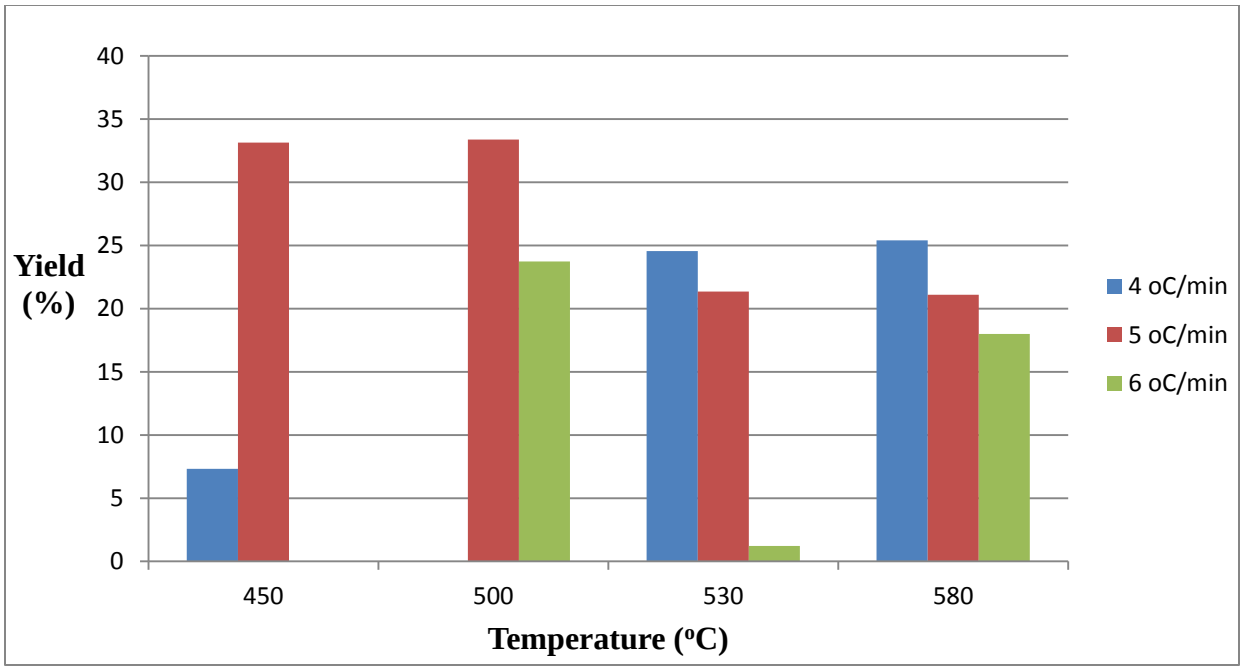


Figure 4.3 Yield of bio-gas at 4, 5 and 6 °C /min heating rates.

At the heating rate of 4 °C /min, the bio-oil yield **(Figure 4.1)** at the final temperatures of 450°C, 530 °C and 580 °C were 38.32 %, 59.44 % and 66.60 % respectively, showing a progressive trend. Concerning the yield of the biochar **(Figure 4.2)** at 4 °C /min, there is a gradual decline which corresponds to 54.36 %, 16 % and 8% at final temperatures of 450°C, 530 °C and 580 °C, respectively. Also, the yield of the incondensable gases **(Figure 4.3)** shows a gradual decline like that of the biochar. At the final temperatures of 450°C, 530 °C and 580 °C, the yield of the incondensable gases are 7.32 %, 24.56 % and 25.40 %, respectively.

These results compare favourably with the 58 wt% yield produced by Hassen-Trabelsi (2014) in his pyrolysis of swine fat. He produced much better yields though, with lamb (77.9 wt%) and poultry (67.6 wt%) fats. Lower yields of bio-oil were recorded with similar type of triglycerides-based wastes: Demirbas (2007) reported 77.1 wt.% with beef tallow at 500 °C; Wiggers et al. (2009) obtained around 73 wt.% for fish oil wastes at 525 °C and Wisniewski et al. (2010) reported 72–73 wt.% yield from waste fish oil pyrolysis. This yield also agrees with results from pyrolysis of different feedstocks: woody biomass (60 - 75 wt.%, Mohan et al., 2006); marine algae (37.5 - 47.4 wt.%, Bae et al., 2011); poly-ethylene based materials (around 86.2 wt.%, Grieco and Baldi, 2012); sewage sludge (27 - 54 wt.%, Fonts et al., 2012).

4.2.2 Effect of Heating Rate on Yield

One of the key objectives of this investigative research was to find out the optimum temperature and heating rate at which the maximum yield of bio-oil would be produced. Keeping the final temperatures at 450, 500, 530 and 580 ^{o}C, and alternating between heating rates of 4, 5 and 6 ^{o}C/min for each temperature, there was a gradual change in the composition of the products.

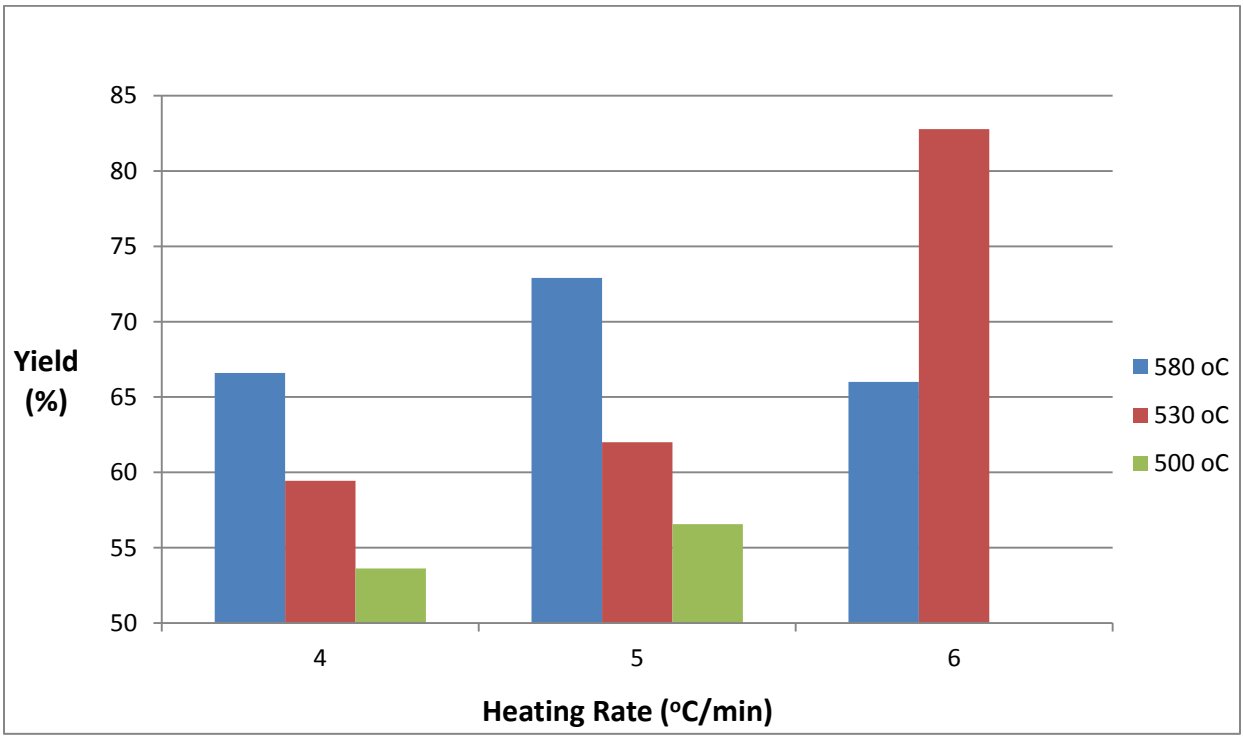


Figure 4.4 Yield of bio-oil at different Final Temperatures

With the final temperature set at 500^{o}C, the yield increased from 53.62 % (B5) to 56.56 % (B6) with increase in heating rate (HR) from 5 ^{o}C /min to 6 ^{o}C /min **(Figure 4.4)**. At a final temperature of 530^{o}C, the same trend continued with yields of 59.44 % (B7), 62 % (B8) and 82.78 % (B9) with corresponding heating rates of 4, 5 and 6 ^{o}C/min. This corresponds to the result of Hassen-Trabelsi et al. (2013) in the pyrolysis of lard where the increase in the pyrolysis temperature from 400°C to 500°C led to a gradual increase in the bio-oil from 54 wt.% to 76 wt.%. Incidentally, at 580^{o}C, there was a decline in the yield thus leaving 82.78 % (B9) as the maximum yield of the pyrolysis experiments. This also corresponds to the result of Hassen-Trabelsi et al. (2013) where there was no significant increase in the bio-oil yield when the temperature was raised from 500°C to 550°C.

4.2.3 Bio-char

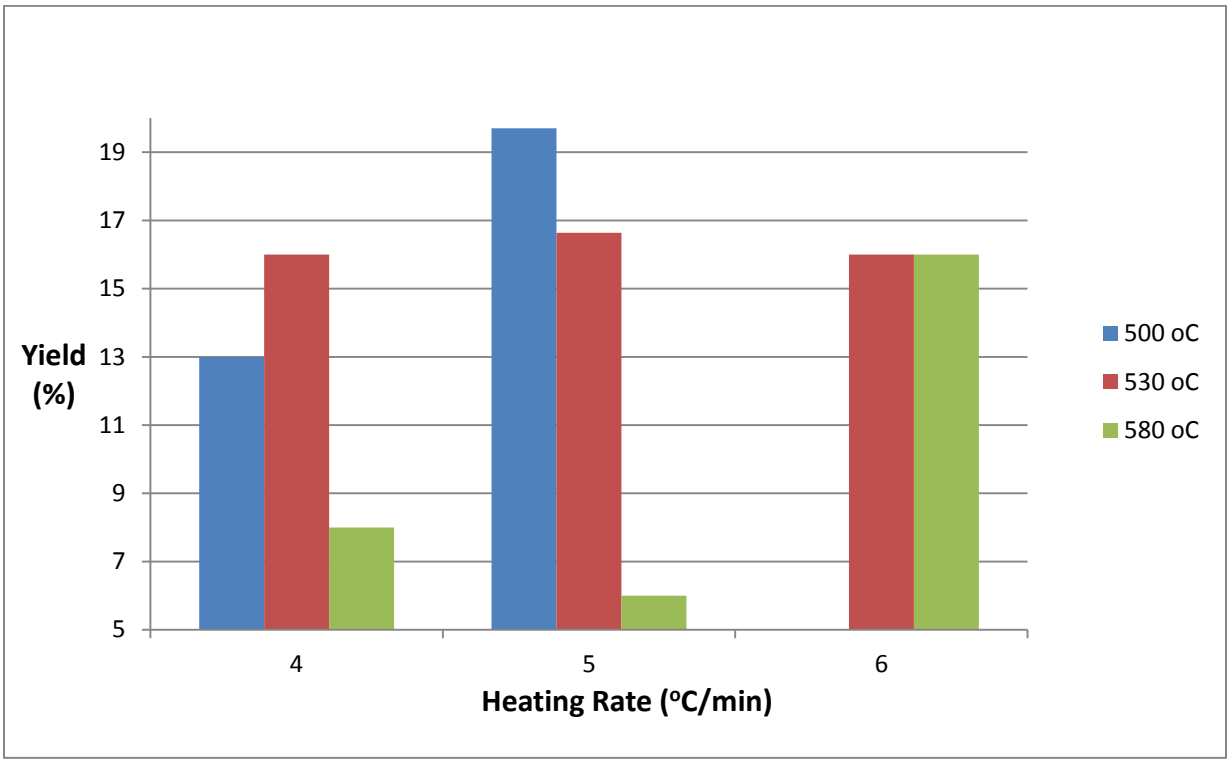


Figure 4.5 Biochar Yield at different Final Temperatures

B1 and B2 resulted in a yield of char and re-condensed bio-oil, hence both values should not be taken as completely bio-char. This is not unexpected considering the relatively low final temperature (450^{o}C) at which they were pyrolyzed **(Figure 4.5)**. The lowest char yield came from B11 (6%) but it did not produce the highest bio-oil yield. This is expected as B11 was pyrolyzed at a higher temperature (580^{o}C) than B9 (530^{o}C) which produced the highest bio-oil yield. The plot of the bio-oil and bio-char yields show an inverse proportionality which is expected – increasing the temperature increases the yield of bio-oil and effects a corresponding decline in the yield of bio-char.

4.2.4 Fatty Acid Methyl Esters

The results of the GC-MS of the samples show a composition of mostly carboxylic acids, esters, alkanes, alkenes, and alkadienes, aromatics. This conforms to the results found by Lima et al. (2004) who studied the chemical composition of pyrolytic products from soybean and castor oils, and Srivastava and Prasad (2000) who reviewed fuel compositions from pyrolysis of triglyceride

materials. **Table 4.4** shows the fatty acid methyl esters that appeared in all the samples and the number of samples they appeared in.

Table 4.4 The most occurring alkyl esters in the bio-oils produced without a catalyst

Name	Weight	Formula	Frequency	CV (MJ/Kg)
9-Octadecenoic acid (Z)-, methyl ester	296	C19H36O2	10	40.16
Docosanoic acid	340	C22H44O2	10	41.06
13-Docosenoic acid, methyl ester, (Z)-	352	C23H44O2	10	41.06
9-Hexadecenoic acid, methyl ester, (Z)	268	C17H32O2	10	39.40
cis-10-Heptadecenoic acid, methyl ester	282	C18H34O2	10	
Decanoic acid, methyl ester	186	C11H22O2	10	36.50
Hexadecanoic acid, methyl ester	270	C17H34O2	9	37.43
Heptadecanoic acid, methyl ester	256	C16H32O2	8	39.18
Phthalic acid, cyclohexyl pentyl ester	318	C19H26O4	8	
Sulfurous acid, Dodecyl 2-ethylhexyl ester	362	C20H42O3S	8	

The alkanes have relatively high calorific values (between 44 MJ/kg – 50 MJ/kg) and appeared in all the samples but their concentration in each of the 12 samples could not be derived due to the tediousness of such calculation. The alkanes that are prevalent in most of the samples are 2-bromo dodecane, eicosane, 2-methyl-heptadecane, 2,4,6-trimethyl-heptane, tetramethyl-silane, tridecane, and hexadecane.

The alkenes that are most common are, 1-methylene-1H-Indene, 1-dodecene, 1-tridecene, 2-tetradecene and 6-tridecene. The alkenes generally have slightly higher calorific values than the alkanes and are formed from the cleavage of the carboxyl side of triglycerides entities, followed by the decarboxylation.

However, the occurrence of carboxylic acids is usually linked to the cleavage of the glycerol moieties (Maher and Bressler, 2007). The most prevalent fatty acid methyl esters in the samples and the number of samples they appeared in are 9-octadecenoic ME (10), docosanoic acid (10), 13-docosenoic acid (10), 7-hexadecenoic acid (10), cis-10-Heptadecenoic acid (10), Decanoic acid (10), and hexadecanoic acid (9). These carboxylic acids have high calorific values and they

generally increase as their carbon chains increase. Their concentration in the bio-oils impacts significantly on the calorific value of each bio-oil.

Hexadecane ($C_{16}H_{38}$) is an alkaline hydrocarbon commonly called Cetane. It appeared in eight (8) of the ten (10) samples. It ignites very easily under compression and is assigned the cetane number of 100 hence it is a reference to the ignition quality of other fuel mixtures. Its presence enhances the fuel nature of the bio-oils especially if its calorific value (47.35MJ/Kg) is considered. Incidentally, B11 recorded the highest concentration of Hexadecane (8998.05 ppm) but a low CV, 33.58 MJ/kg, which is 64% of CV of B12 (52.41 MJ/kg), the highest. Meanwhile, B12 recorded a Hexadecane concentration of 5753.48 ppm, which is 64% of its concentration in B11. The absence of Hexadecane in samples B7 and B8 could explain their recording two of the three lowest calorific values - 31.80 and 32.01 MJ/Kg respectively. But its concentration does not predict the calorific values of the samples. The lowest recorded CV, 29.86 MJ/kg is from B6 with a Hexadecane concentration of 5753.80 ppm, the third highest.

Apart from Hexadecane, the other sizeable components in B12 are 2,6,8-trimethyldecane (3651.13 ppm) and Eicosane (1369ppm). 2,6,8-trimethyldecane, with a total of C_{13} predictably has a low CV of 10.56MJ/Kg while Eicosane, an alkane with a CV of 47.23 MJ/kg seem to have greater impact on the total CV of the sample. Hexadecane, Eicosane and 2,6,8-trimethyldecane appeared in all the samples except in B7 and B8, which incidentally recorded the two lowest CVs of the whole experiment. Considering that the FT of B7 and B8 is 530 ^{o}C, it is deductible that their FT was too low for the depolymerization of the molecules that could only be broken down at higher temperatures.

The formation of the aromatic moieties in the samples is generally attributed to secondary reactions - cyclization of olefin structures and Diels–Alder reactions. 1,2,3,4-tetramethyl benzene, tert-butyl benzene and p-cymene are the aromatics that appeared in all the samples except B7 and B8.

4.2.5 Analysis of Bio-oils Properties

Table 4.5 Properties of the pyrolysis bio-oil samples

	pH	A.V.	Ash	C	H	N	S	O	Viscosity	Density	C.V
			%	%	%	%	%	%	mm^2/s	g/cm^3	MJ/ Kg
B1	4.62	204.00	4.39	85.13	11.87	0.91	0.41	2.09	13.97	0.78	34.47
B2	3.99	194.95	3.84	74.10	11.78	0.53	0.00	13.59	10.76	0.81	37.80
B5	4.69	171.33	4.50	75.41	11.44	0.62	0.00	12.53	10.63	0.83	38.21
B6	4.05	125.88	3.25	75.40	11.88	0.53	0.00	12.19	9.75	0.79	29.86
B7	4.22	129.32	3.50	73.57	11.68	0.00	0.00	14.75	9.62	0.80	31.80
B8	3.78	166.22	3.44	79.79	11.55	0.05	0.00	8.60	9.56	0.78	32.01
B9	4.01	179.52	4.42	75.27	11.67	0.54	0.00	12.52	9.56	0.79	39.09
B10	4.07	179.52	6.41	75.38	11.86	0.24	0.00	12.22	7.17	0.78	35.70
B11	3.67	170.85	1.28	74.21	11.52	0.34	0.00	13.93	6.97	0.80	33.58
B12	4.70	180.87	2.66	74.51	11.66	0.38	0.00	13.45	6.79	0.68	52.41

B12 (580^{o}C & 6 ^{o}C/min) produced the highest Calorific Value (52.41 MJ/kg). This exceeds the typical CVs of biodiesels (39–41 MJ/kg), gasoline (46 MJ/kg), diesel (43 MJ/kg), petroleum (42 MJ/kg), and coal (32–37 MJ/kg) (Demirbas, 2008). It is also higher than the 41 MJ/kg obtained by Beis et al. (2002) from safflower seed, the 36.4 MJ/kg obtained by Ozcimen and Karaosmanoglu (2004) from rapeseed cake and the 40 MJ/kg obtained by Adebanjo et al. (2005) from lard. The lowest CV (29.86 MJ/kg) came from B6 (500^{o}C & 6^{o}C/min). Incidentally, both samples were produced at 6^{o}C/min HR. B12, however, recorded the lowest density (0.675 g/cm^3) which might explain, partly, its extraordinarily high CV, as an inverse relationship exists between density and CV. The others recorded average CVs, ranging between 31 – 39 MJ/kg and with a relatively higher density (0.77 – 0.83 g/cm^3).

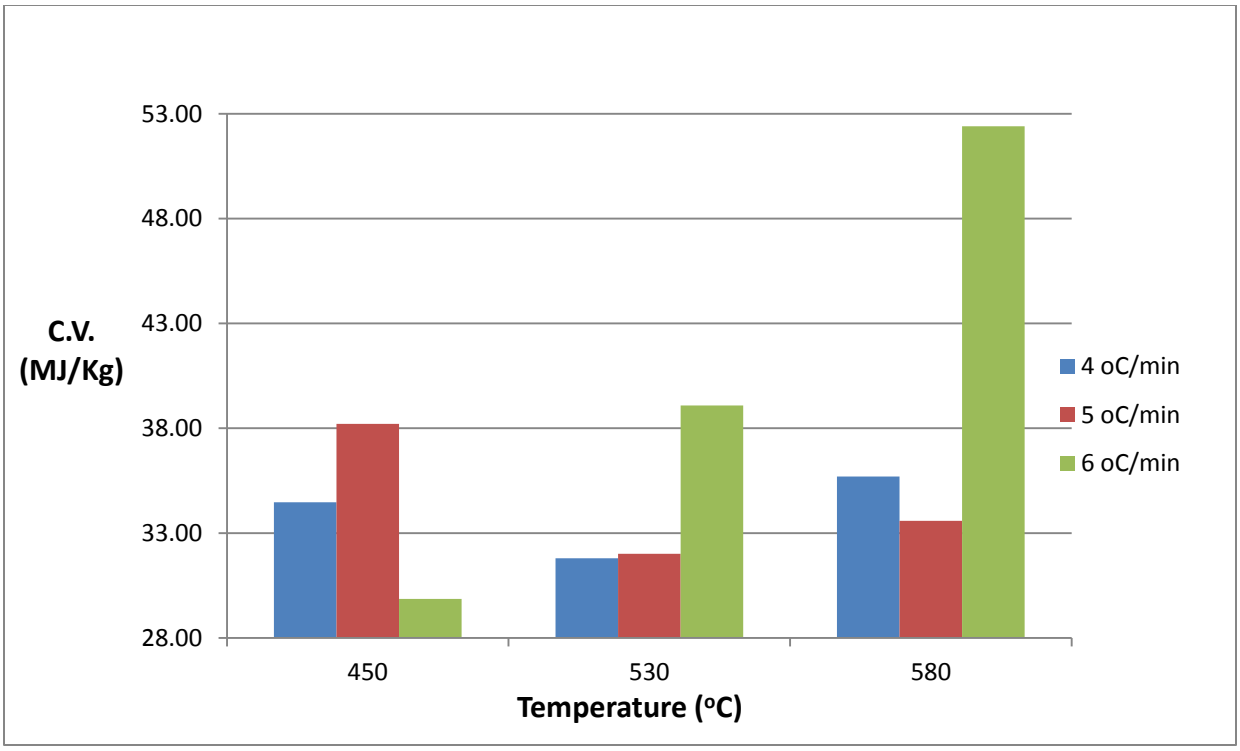


Figure 4.6 Calorific Value of Bio-oil at 4, 5, and 6°C/min HR

The pH of the samples ranging from 3.46 – 4.80, indicate mild acidity which conforms to literature, but are better than, 2.5 from wood-derived crude bio-oil by Bridgwater (2012), 2.6 from pine bio-oil, and 2.8 from hardwood bio-oil (Sipila et al., 1998), 2.4 – 2.8 obtained by Oasmaa and Czernik (1999) and the 2.5 by Mohan et al. (2006). This mild acidity could stem from the presence of organic acids during biopolymer degradation (Bridgwater, 2012). Reducing the retention time to forestall secondary reactions would help to thwart this molecular depolymerization.

The samples' densities range from 0.68 to 0.83 g/cm^3. The specification for South Africa petrol diesel SANS 342-2006 is 0.80 g/cm^3 minimum. Virtually all the samples meet this specification except B1 (0.78), B6 (0.79), and B8 (0.78) which are very close. This problem could be solved by reducing the amount of water in the tallow prior to introduction into the reactor as increased water content lowers density. The other source of water in the bio-oil is through the reactions that occur during pyrolysis. These reactions are complex and are not easily controlled.

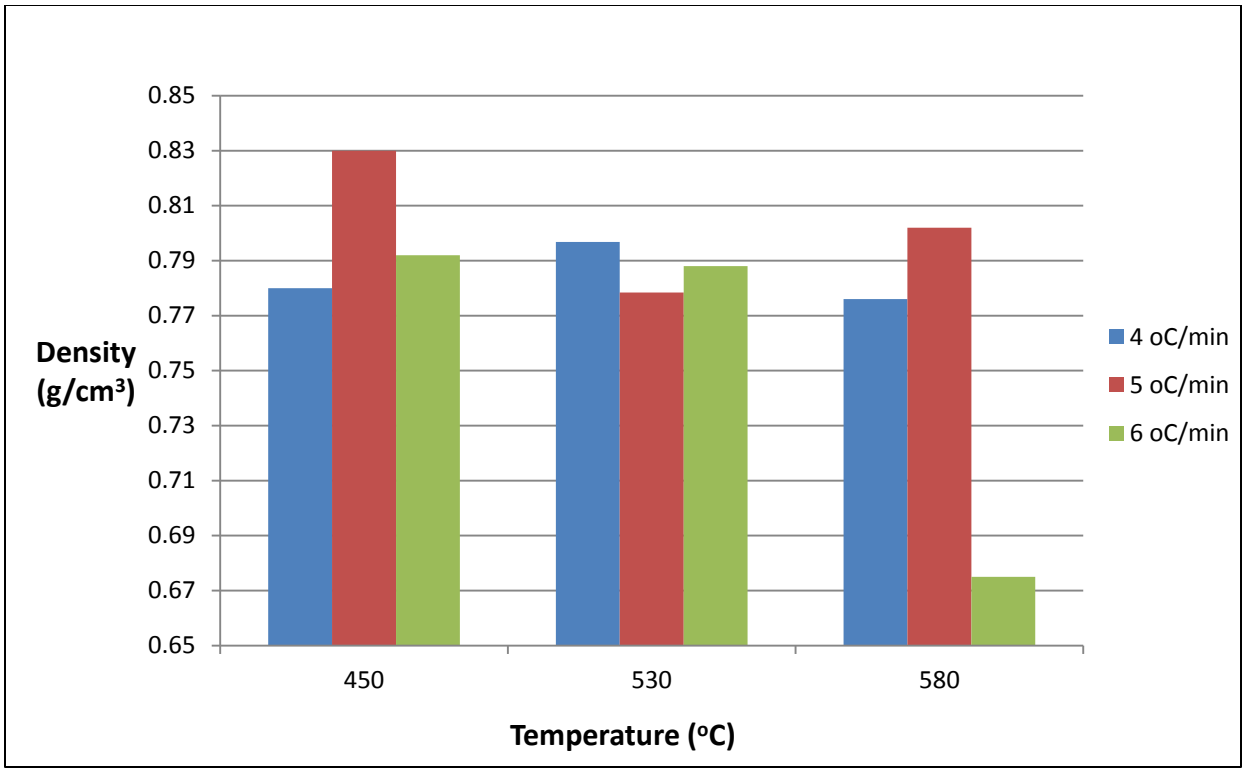


Figure 4.7 Density of Bio-oil at 4, 5, and 6 °C/min HR

The carbon content of the samples are in the high range, 74 – 76 % but B1 have an abnormally high 85.13 %. This partially explains the moderately high CVs of the samples.

This abnormally high N_2 in the samples - 0.24 % to 0.91 % is the nitrogen used as the carrier gas during the experiments. There was no N_2 in the feedstock.

In **Figure 4.8**, high Acid Values (AV) ranging from 125.88 (B6) – 204 mg KOH/g (B1) highlights the presence of free fatty acids in the samples. While this conforms to results from other researchers (107 – 142 mg KOH/g by Wiggers et al., 2009), it is way above the specification (0.80 mg KOH/g maximum) for the B100 (ASTM D 6751 – 02). This could be remedied by acid esterification - treating the oil with an alcohol in the presence of acid catalyst. The optimum conditions that could reduce FFA content in the feedstock to less than 1.88% (acid value 3.76 mg KOH/g waste cooking oil) were 50 °C, 20% methanol to oil ratio (by volume) and 0.4 vol.% H2SO4 after 5 h (Ding et al., 2012).

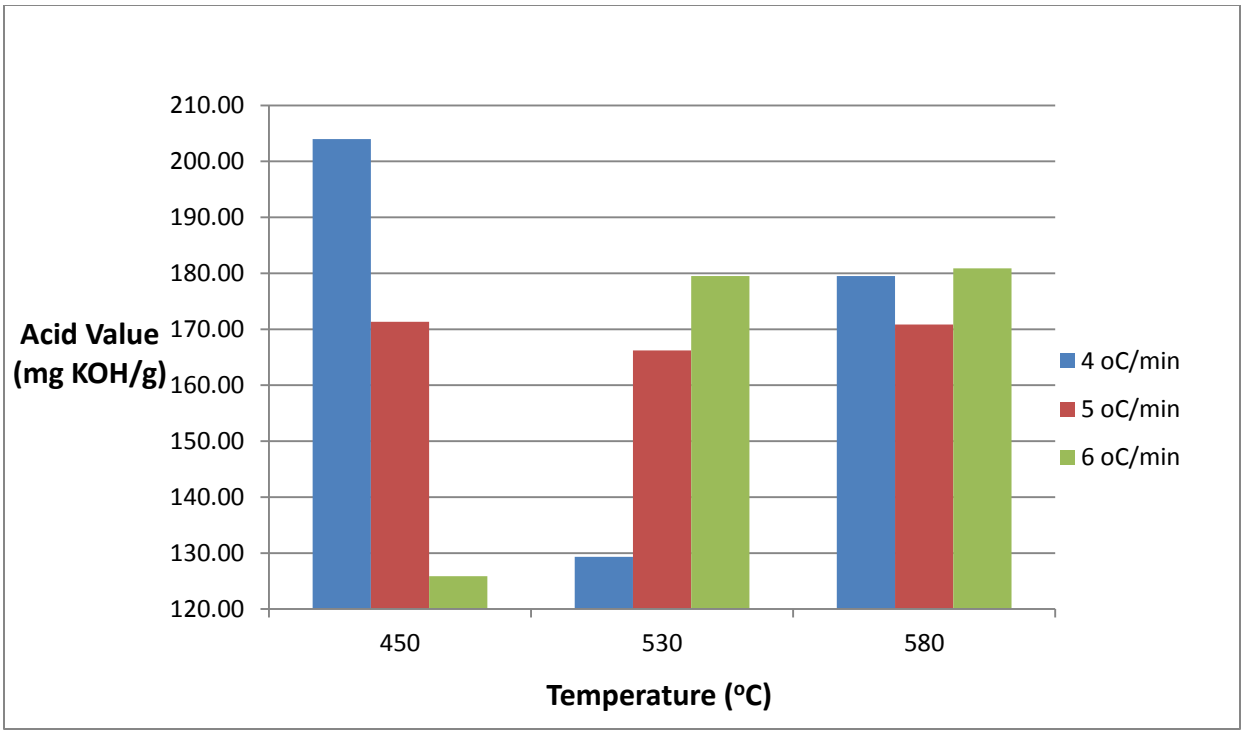


Figure 4.8 Acid Values of Bio-oil at 4, 5, and 6 °C/min HR

There is a remarkably consistent amount of hydrogen in all the samples, ranging between 11.44 – 11.88 %. This conforms to the hydrogen content of heavy fuel oil. These hydrogens could have been as a result of either of formation of cycloolefins and aromatics, polymerization of olefins and aromatics, polycondensation of triglyceride, splitting of hydrocarbons, and dehydrogenation of olefins (Adebanjo et al, 2005).

The trace amount of sulphur in the samples is as a result of the quantity in the feedstock. Naturally, the combustion product would contain trace amounts of the SO*x* pollutants. Potential problem is that it will lead to catalyst poisoning during upgrading.

The ash contents of the samples range from 1.28 – 6.41 % m/m which is well above the South African specification of 0.01 % m/m for petrol diesel SANS 342-2006 and a great handicap of the bio-oil. The inherent problems are aging of the oil, sedimentation, filter blockage, catalyst blockage, engine injector blockage, alkali metal poisoning. Hot-vapour filtration can reduce this ash content of the oil to less than 0.01% (Bridgwater, 2012).

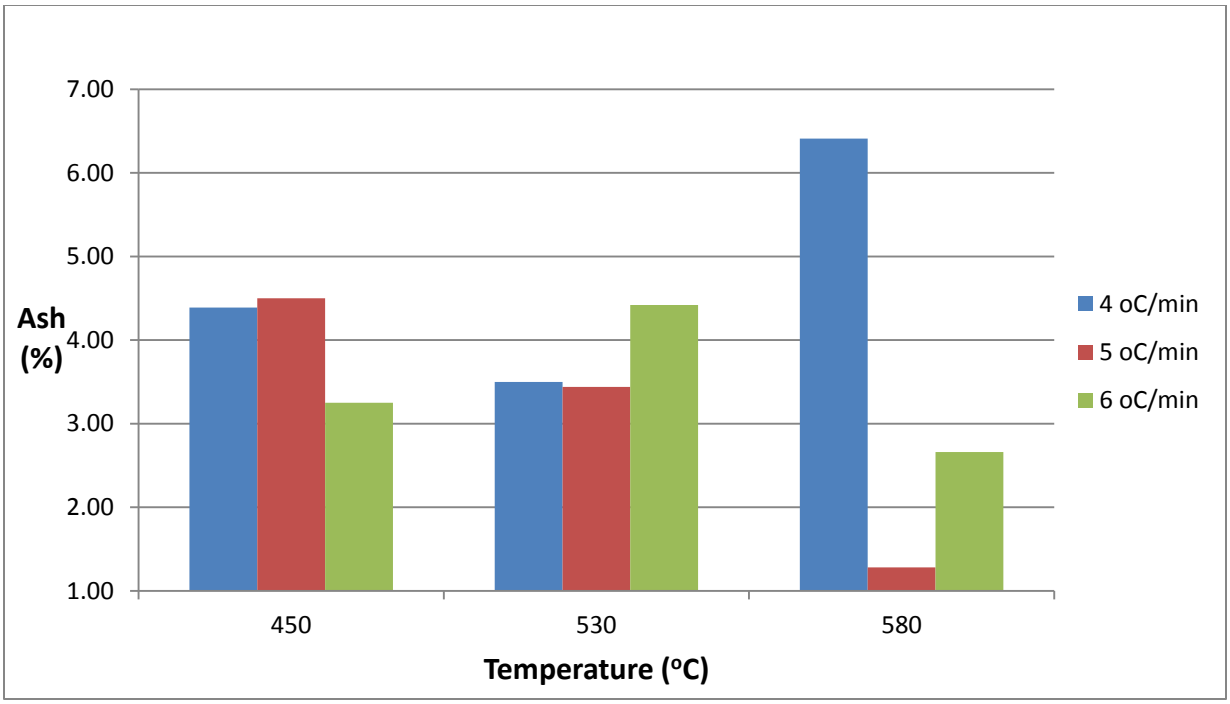


Figure 4.9 Ash Content of Bio-oil at 4, 5, and 6 °C/min HR

Most of the samples recorded O_2 values in the range of 12 % to 14 % except B1 and B8 with very low values, 2.09 and 8.60 respectively. B12 recorded a moderate 13.45%. These values are far better than the 35-40% O_2 content as stated by Oasmaa and Czernik (1999) which reduces considerably, the potential danger of instability caused by oxidation as it improves the combustion efficiency.

There is progressive decline in the viscosity of the samples as the temperature and heating rates are increased. All the samples recorded viscosities (6.79 – 13.97 mm^2/s) which are above the range of the specification of the South African specification of 2.2 – 5.3 mm^2/s for petrol diesel SANS 342-2006. At 500°C FT and 5 °C/min HR bio-oil of viscosity, 10.63 mm^2/s was produced but the bio-oil of 6°C/min HR recorded 9.75 mm^2/s. Likewise, at 530 °C, samples produced at 4°C/min, 5 °C/min and 6°C/min recorded viscosities of 9.62, 9.56 and 9.56 mm^2/s respectively.

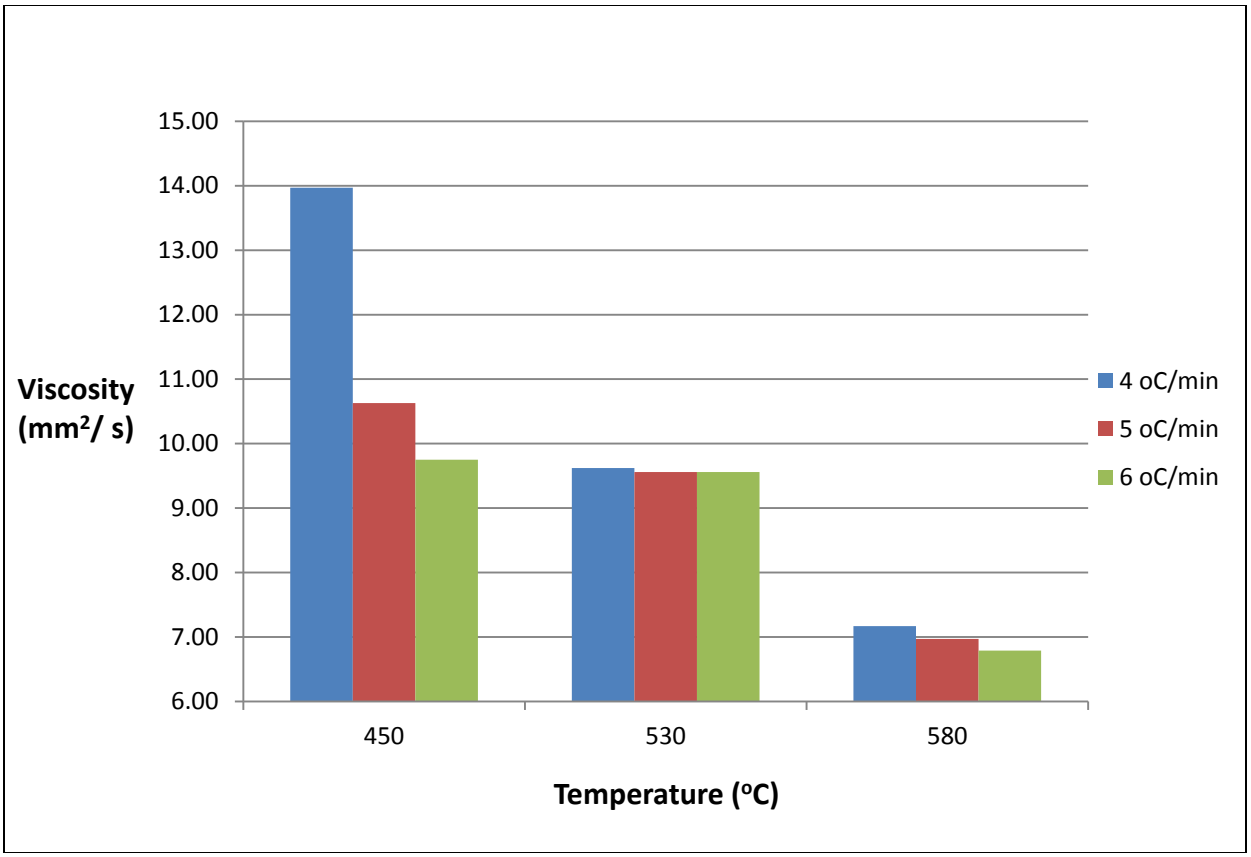


Figure 4.10 Viscosity of the Bio-oils at 4, 5, and 6°C/min HR

Significantly, B12, which recorded the highest calorific value (52.41 MJ/Kg) recorded the lowest viscosity, 6.79 mm^2/s. Water addition would help to reduce this viscosity values but there is a limit to the amount of water which can be added to the liquid before phase separation occurs. Also, water addition does improve stability but it reduces heating value. Bio-oil's miscible with polar solvents such as methanol, acetone, etc. would help reduce viscosity but it would also increase cost of production.

4.3 EFFECT OF ZEOLITE CATALYST ON THE PYROLYSIS EXPERIMENT

Table 4.6 The result of the pyrolysis experiments with Zeolite nano-catalyst.

PYROLYSIS WITH ZEOLITE CATALYST AT 6 ^{o}C/min HEATING RATE							
	Final Temp	Volume of Biofuel produced	Mass of Biofuel produced	Yield of Bio-oil	Mass of Char Produced	Mass of Incondensable gases	% Zeolite and Remark
	^{o}C	cm^3	g	%	g	g	
C1	530	35	29	58.00	10	11.00	0.5g (1%) - Sludge in tube
C2	500	33	28	56.00	11	11.00	0.5g (1%) - Sludge in tube
C3	530	33	27	54.00	8	15.00	1g (2%) - Sludge in tube

An initial 1% zeolite was used in the pyrolysis experiment at a maximum temperature of 500 ^{o}C and it resulted in a yield of 56% (C2). With the zeolite quantity kept at 1% but the final temperature raised to 530 ^{o}C, a yield of 58% (C1) was achieved. When the zeolite quantity was then raised to 2%, the yield reduced to 54% (C3). Therefore, instead of improving the yield, zeolite inhibited any increase in yield, and with a high degree of coking and gas formation as stated by Twaiq et al. (1999).

There was no marked change in the mass of biochar and incondensable gases produced. C1 and C2 recorded identical values for the incondensable gases – 11g, while the difference in the mass of biochar – 10 g for C1 and 11 g for C2, is negligible.

Table 4.7 Properties of the samples of the pyrolysis with zeolite catalyst.

Sample	pH	Acid Value	Ash	C	H	N	S	O	Viscosity	Density	C.V
		mg KOH/g	%	%	%	%	%	%	mm^2/s	g/cm^3	MJ/Kg
C1	4.11	121.44	3.34	73.89	11.30	0.34	0	14.81	6.25	0.55	35.47
C2	4.08	121.86	3.36	74.07	11.31	0.36	0	14.23	6.33	0.55	35.40
C3	4.11	125.88	3.33	74.39	11.46	0.36	0	13.78	6.31	0.55	35.21

The acid values (121.86 – 125.88) are lower than all the samples produced without a catalyst except for B6 which recorded 125.88, the same as C3. This anomaly could have occurred because B6 is produced at 500^{o}C while C3 at 530^{o}C – increase in temperature causes an increase in acidity due to increased dehydration.

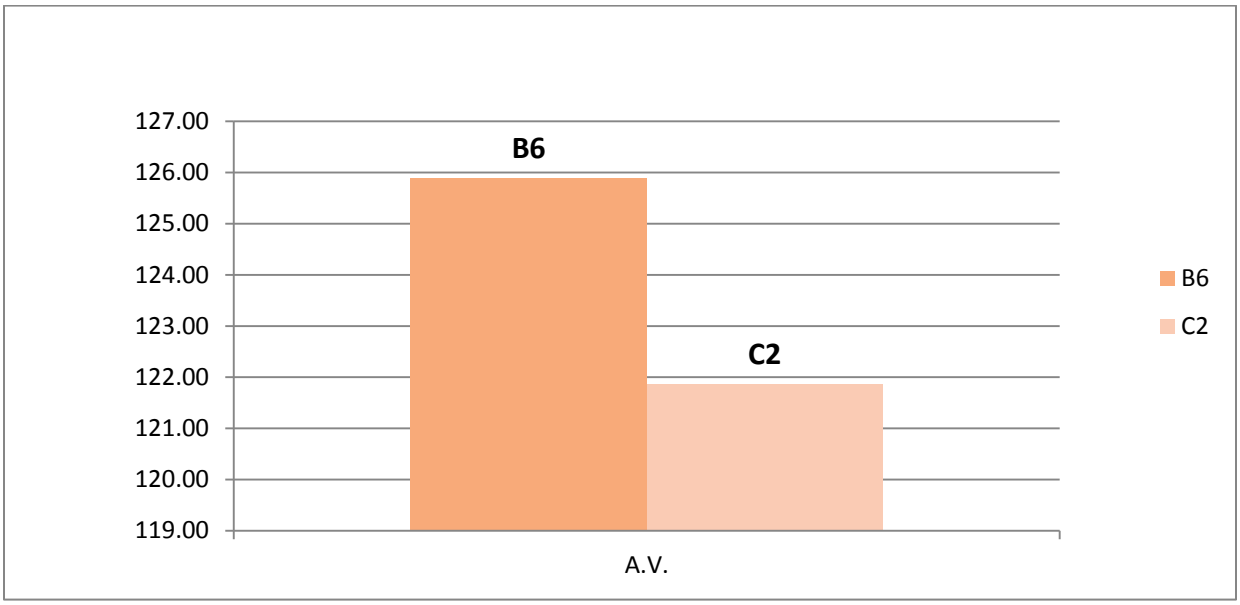


Figure 4.11 Acid Value of Bio-oils of B6 and C2 produced at 500^{o}C and 6^{o}C/min

Both B6 and C2 were produced at 500^{o}C FT and 6 ^{o}C/min HR but with C2 produced with 1% zeolites **(Figure 4.11)**. C2 showed a minor 3% reduction in the acid value.

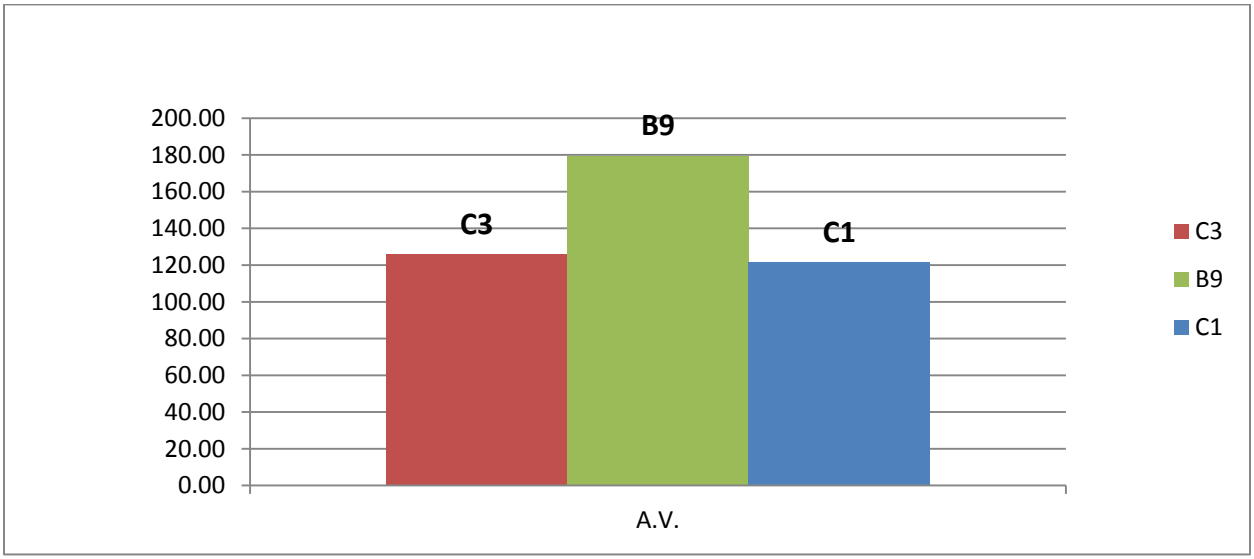


Figure 4.12 Acid Value of Bio-oils of B9, C1 & C3 produced at 530^{o}C and 6^{o}C/min

But when the FT is increased to 530^{o}C and the zeolites's quantity is increased to 2% in C3 **(Figure 4.12)**, C1 recorded a significant 32% reduction while C3 recorded an equally significant 30% reduction in the acid value. This paradox in the reduction of the acid value as the amount of zeolites is increased could likely have emanated from the acidic nature of zeolites (Weitkamp, Jens, 2000). Also, the values of the samples produced with 1% zeolites – C1 (121.44) and C2 (121.86), are much lower than the sample produced with 2% zeolites – C3 (125.88). This attests to the acidic nature of zeolites (Guo and Fang, 2011) even though it reduced the acidity of the bio-oil considerably. All these values are far above the specified value of 0.80 mg KOH/g maximum for the B100 (ASTM D 6751 – 02).

The pH values (4.08 – 4.11) are in the same range as those samples obtained without a catalyst.

The viscosities are in the range, 6.25 – 6.31 mm^2/s, and much lower than most of the bio-oils produced without a catalyst, which are in 6.79 - 13.97 mm^2/s. All of these values fall above the specification for South Africa petrol diesel SANS 342-2006 of 2.2 cSt – 5.3 cSt. (cSt = mm^2/s).

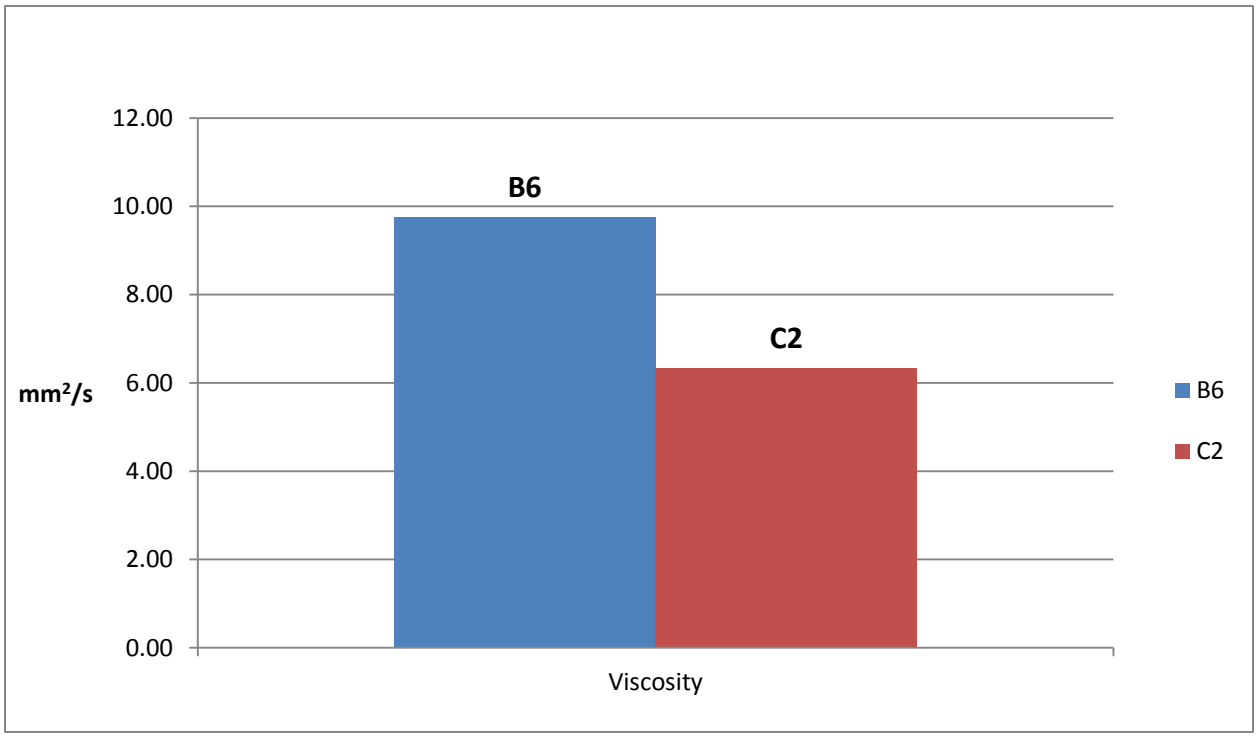


Figure 4.13 Viscosity of Bio-oils of B6 & C2 produced at 500^{o}C and 6 ^{o}C/min

As shown in **Figure 4.13**, both B6 and C2 were produced at 500^{o}C and 6 ^{o}C/min but only 1% zeolites was added into C2. The result is a massive 35% reduction in viscosity.

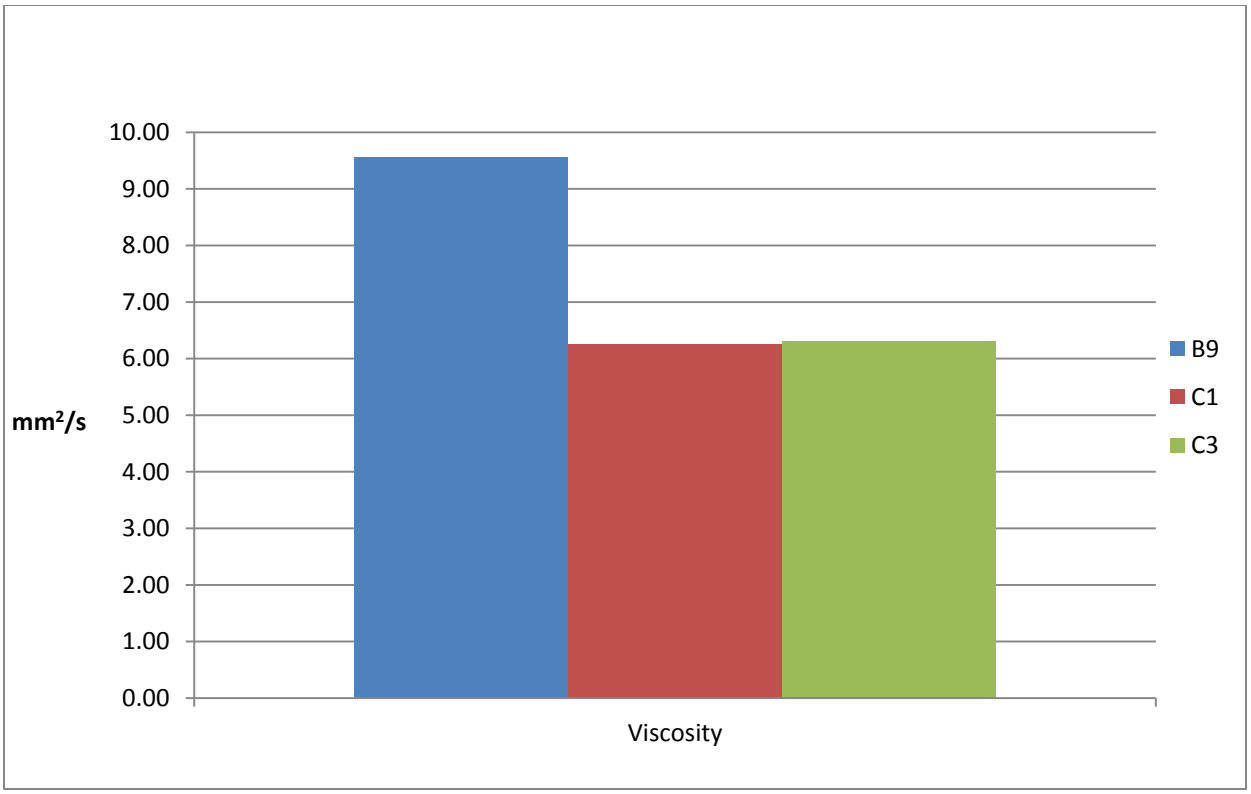


Figure 4.14 Viscosity of Bio-oils of B9, C1 & C3 produced at 530 ^{o}C and 6^{o}C/min

And as can be seen from **Figure 4.14**, B9, C1 and C3 were produced at 530^{o}C and 6 ^{o}C/min but 1% and 2% zeolites were used in C1 and C3 productions respectively. The change from C1 to C3, a 0.96% increase, is minor though not without reckoning. Hence the increase in the zeolites quantity, from 1% to 2% increased the viscosity, but only slightly. But what is worthy of note is the increase in viscosity when C1 and C3 are compared to B9. C1 recorded a 35% reduction to B9 while C3 recorded a 34% reduction to B9.

The ash content, 3.33 – 3.36 % is similar to those samples produced without a catalyst, and which are above the specification of 0.01 % m/m for South Africa petrol diesel SANS 342-2006. The samples have identical densities, 0.55 g/cm^3 which is below the 0.80 g/cm^3 minimum specification for South Africa petrol diesel SANS 342-2006.

The values of the elemental components remained almost the same for all three samples and close to the values recorded for the bio-oils produced without a catalyst but the latter set of samples showed a wider range of values for Carbon, Nitrogen and Oxygen.

Table 4.8 Methyl esters of significant concentration in bio-oils produced with a catalyst

Name	Weight	Formula	CV (MJ/Kg)
5,8,11,14,17-Eicosapentaenoic acid, methyl ester, (all-Z)-	316	C21H32O2	
7-Hexadecenoic acid, methyl ester, (Z)-	268	C17H32O2	
Heptanoic acid, methyl ester	130	C6H10O3	31.89
Pentanoic acid, 5-oxo-, methyl ester	130	C6H10O3	21.83

Table 4.8 shows the methyl esters that appeared in the three samples with significant concentrations. The highest concentration in all three samples was 5877.25 ppm of pentanoic acid, 5-oxo-, methyl ester in C2 followed by 1146.98 ppm of heptanoic acid, methyl ester in C3 but since they recorded identical CVs (35.21 – 35.47 MJ/Kg), the concentrations of these components loses much of their significance. Nevertheless, there is a cluster of cyclo-olefins - 4,4-dimethyl-cyclohexene, butyl-cyclohexane, butyl-cyclopentane, 1-pentyl-cyclopentene, etc. which are formed from the cyclization of C=C bonds present in unsaturated acids, and cycloparaffins produced by the addition of proton to cycloolefins (Adebanjo et al., 2005). These cyclo-olefins have CVs that are comparative to alkyl esters and alkanes. Aromatic hydrocarbons - 2-propenyl-benzene, 1-ethenyl-2-methyl-benzene, 1-methyl-4-propyl-benzene - were formed from thermal reaction of olefins and diolefins, aromatization reactions, and hydrogen elimination from C_{6+} cycloolefins at high temperature (Adebanjo et al., 2005).

4.4 ECONOMIC IMPACT ASSESSMENT OF BIO-OIL PRODUCTION FROM ABATTOIR WASTE

Consider that the typical amount of residues produced by an abattoir from a cattle is 45% (wt/wt) and they contain approximately 15% fat (Feddern et al. 2011). Karan Beef (abattoir in this investigation) slaughters about 1200 heads of cattle per day (Karan Beef, 2015) and since the average weight of a cattle is 753 kg, they would be producing,

1200 X 753 X 0.45 X 0.25 = 101,655 kg of fat per day.

For a high yield of 82.78% of bio-oil produced during the pyrolysis experiments,

101,655 X 0.8278 = 84 150.01kg of bio-oil would be produced.

This will produce an equivalent of,

84 150.01 kg X 39.09 MJ/Kg = 3,289,423.85 MJ of Biofuel.

Converting it to Watts,

$P_{(W)} = E_{(J)} / t_{(s)} =$ 3,289,423,850,000 / 86400 = 38072035 Watts per day

= 38072035 / 24 = 1586334.79 Watts per hour

= 1586 kWh per day

Factoring in the electric power transmission and distribution losses (% of output) in South Africa and using the 2011 value of 8.47% (www.indexmundi.com),

1586 X (1 - 0.0847) = 1451.67 kWh per day

And in a 22-day month, they will produce

1451.67 X 22 = 31,936.74 kWh per month.

According to Agriculture and Horticulture Development Board (AHDB, 2013), it costs about 50Kwh to process a cattle. Therefore,

1451.67 KWh per day will process,

1451.67 /50 = approx. 29 cattles per day.

At an Eskom electricity rate of R1.48 per KWh (Eskom, 2016), the company would have saved,

R1.48/KWh X 1451.67 KWh = R2,148.47

And in a month of 22 working days, they would save,

. R2,148.47 X 22 = R47, 266.38

If you consider a township like Diepsloot in the north of Johannesburg, with a population of about 350,000 people (www.diepsloot.com), and considering that an average household contains four (4) people, then Diepsloot will have,



Figure 4.15 **Diepsloot** (http://www.joburg.org.za)

350 000/4 = 87 500 households.

If an average household uses the following per day:

• Electric bulb	=	60W X 5h	= 300 Wh
• Small Hotplate	=	1275W X 0.2h	= 255 Wh
• Kettle	=	1900W X 0.3h	= 570 Wh
• Iron	=	1235 X 0.4h	= 494 Wh
• TV	=	50W X 6h	= 300 Wh
		TOTAL	1919 Wh

So, if a household uses 1.9 kWh (1919Wh) in a day, then in a month, it will use,

1.919 X 30 = 57.57 kWh per month

From (1) above, Karan Beef could produce enough energy to take care of,

31,936.74 kWh / 57.57 = 554.75 households every month.

And when you factor in the 87 500 households of Diepsloot, the number of abattoirs of Karan Beef size that would supply the electricity need of Diepsloot is,

87 500 / 554.75 = 157.73 abattoirs.

It wouldn't be too difficult to find the approximately 158 abattoirs within the 479 registered abattoirs in South Africa (Neethling, 2014) to supply the electricity need of Diepsloot. This will have a huge impact in the following ways:

- It will halt the adverse effect on the environment caused by the traditional disposal of waste fat and considerably reduce the harmful effect of other abattoir wastes.
- It will enhance the "green" status of South Africa globally.
- About its greatest impact is the relief it will bring to the country's national electricity grid. Considering that electricity theft is high in South Africa and prevalent in places like Diepsloot which is littered with informal settlements, this project will obliterate the theft of electricity and drastically reduce the theft of the accompanying infrastructure.
- It will crush crime which thrives on darkness. Street lights would light up the place.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Production of biofuel from waste animal fat using the pyrolysis (thermal cracking) method was achieved with the highest yield of bio-oil (82.78 %) obtained at 530^{o}C final temperature and 6^{o}C/min heating rate with the sample recording a calorific value of 39.09 MJ/Kg. The bio-oil with the highest calorific value, 52.41 MJ/Kg was produced at 580^{o}C FT and 6^{o}C/min HR. In the absence of a catalyst, the yield of bio-oil declined after it reached the optimum value of 82.78 % with further increase in temperature beyond 530^{o}C.

Some of the properties of the bio-oils produced – carbon, hydrogen, sulphur, oxygen, density and calorific value conformed to the specification of South Africa petrol diesel SANS 342-2006 and/or Biodiesel (B100) specification - ASTM D 6751 – 02 requirements, where the specification is not stated, as to be used as a transport fuel. However, the values for pH, acid value, ash % and viscosity were found to be outside the South Africa petrol diesel SANS 342-2006 specification, hence unacceptable. The zeolite catalyst (Zeolite 96096) did not improve the yield of the bio-oil, but stimulated a marked improvement in some of the bio-oils' properties. The viscosity improved by 35% for each of the samples produced with 1% zeolite and 34% for those produced with 2% zeolite. Once again, the properties of the bio-oils produced were compared to the South Africa petrol diesel SANS 342-2006 specification – carbon, hydrogen, sulphur, oxygen, density and calorific value and were found to conformed to the specification required for South Africa petrol diesel SANS 342-2006, or where the specification is not stated, are of acceptable values as to be used as a transport fuel. The pH, acid value, ash content, nitrogen %, and density did not conform to the specification required for South Africa petrol diesel SANS 342-2006 and would need to be improved.

5.2 RECOMMENDATIONS

In order to improve the yield and quality of the biofuel produced so that it could be used directly in automobiles, further work needs to be done:

1. A catalyst that will improve the quality of the bio-oil produced so that it would be suitable as a fuel for automobiles needs to be found and investigated.
2. To improve the yield of the bio-oil to values above 90% through adjustment of the operational conditions needs to be investigated. One possible method is to increase the carrier gas flow rate with rise in temperature to ensure that increase in the residence time when the vapour volume inside the pyrolysis reactor is increased would ensure complete molecular depolymerization but hinder commencement of secondary reactions.
3. Improvement of the yield of the bio-oil should be investigated through the use of a basic catalyst that will further reduce the acid value and viscosity but increase the density of the bio-oil produced. This has to be a catalyst that can withstand temperatures above 350^{o}C.
4. Recovery of the catalyst should be attempted.
5. Characterization of the incondensable gases and the bio-char should be done with a view to assessing their usage as energy sources for heating the pyrolysis reactor.

REFERENCES

Adebanjo, A.O., Dalai, A.K. and Bakhishi, N.N. (2005) 'Production of diesel like fuel and other value-added chemicals from the pyrolysis of animal fat', *Energy Fuels,* vol. 19, pp. 1735–1741.

Agriculture and Horticulture Development Board (AHDB), (2013). *Resource Use in the British Beef and Lamb Processing Sector*. Available: www.beefandlamb.ahdb.org.uk/wp/wp-content/uploads/2013/04/resourceenergy_100211-factsheet-4.pdf [21/02/2106].

Alencer, J. W., Alves, P. B. and Craveiro, A. A. J. (1983) 'Pyrolysis of tropical vegetable oils', *Journal of Agricultural and Food Chemistry*, vol. 31, no. 6, November, pp. 1268-1270.

Altafini, C.R., Wander, P.R. and Barreto, R.M. (2003) 'Prediction of the working parameters of a wood waste gasifier through an equilibrium model', *Energy Conversion Management*, vol. 44, pp. 2763–2777.

Aniebo, A.O., Wekhe, S.N. and Okoli, I.C. (2009) 'Abattoir Blood Waste Generation in River State and its Environmental Implications in the Niger Delta', *Toxicological & Environmental Chemistry,* vol. 91, no. 4, June, pp. 619-625.

Asadullah, M., Rahman, M.A., Ali, M.M., Rahman, M.S., Motin, M.A., Sultan, M.B. and Alam, M.R. (2007) 'Production of bio-oil from fixed bed pyrolysis of bagasse', *Fuel,* vol. 86, no. 16, pp. 2514–2520.

Astruc, D., Lu, F. and Aranzaes, J. R. (2005) 'Nanoparticles as recyclable catalysts: The frontier between homogeneous and heterogeneous catalysis', *Angewandte Chemie* International Edition, vol. 44, pp. 7852–7872.

Babu, B.V. (2008) 'Biomass pyrolysis: A state-of-the-art review. *Biofuels, Bioproduct & Biorefining*, vol. 2, August, pp. 393–414.

Bae, Y.J., Ryu, C., Jeon, J.K., Park, J., Suh, D.J., Suh, Y.W., Chang, D. and Park, Y.K. (2011) 'The characteristics of bio-oil produced from the pyrolysis of three marine Macroalgae', *Bioresource Technology*, vol. 102, no. 3, February, pp. 3512–3520.

Bala B.K. (2005) 'Studies on biodiesels from transformation of vegetable oils for diesel engines', *Energy Education Science Technology*, vol. 5, pp. 1–45.

Barker, S.N. (1996) 'Gasification and pyrolysis - routes to competitive electricity production from biomass in the UK', *Energy Conversion and Management*, vol. 37, no. 6-8, Proceedings of the International Energy Agency Greenhouse Gases: Mitigation Options Conference, pp. 861–866.

Beis, S. H., Onay O. and Kockar, O. M. (2002) 'Fixed-bed pyrolysis of safflower seed: Influence of pyrolysis parameters on product yields and compositions', *Renewable Energy*, vol. 26, issue 1, pp. 21–32.

BP (2013). BP Energy Outlook 2030 Report. London, United Kingdom. Available: http://.www.bp.com/content/dam/bp/pdf/statistical-review [19 September 2015].

Bridgwater, A.V., Meier, D. and Radlein, D. (1999) 'An overview of fast pyrolysis of biomass', *Organic Geochemistry*, vol. 30, pp. 1479–1493.

Bridgwater, A.V. and Peacocke, G.V.C. (2000) 'Fast pyrolysis processes for biomass', *Renewable and Sustainable Energy Reviews*, vol. 4, pp. 1–73.

Campbell, I.M. (1983) *Biomass, Catalysts and Liquid Fuels*, London: Holt, Rinehart and Winston.

CANMET Energy Technology Center, Canada (2004) *Super Cetane Technology*. Available: http:///www.nrcan.gc.ca/es/etb/cetc/cetc01/htmldocs/factsheet_supercetane_e.html
[May 10, 2004].

Chang, C. C. and Wan, S.W. (1947) 'China's Motor Fuels from Tung Oil', *Industrial and Engineering Chemistry*, vol. 39, no. 12, December, pp. 1543-1548.

Chukwu, O., Adeoye, P.A. and Chidiebere, I. (2011) 'Abattoir wastes generation, management and the environment: a case of Minna, North Central Nigeria', *International Journal of Biosciences,* vol. 1, no. 6, pp. 100-109.

Craig, W. and Coxworth, E. (1987) 'Conversion of vegetable oils to conventional liquid fuel extenders', In: Granger, C., editor, *Proceedings of the Sixth Canadian Bio-energy Research and Development Seminar*, Richmond, Canada, February, pp. 407–411.

Dandik, L. and Aksoy, H.A. (1998) 'Pyrolysis of used sunflower oil in the presence of sodium carbonate by using fractionating pyrolysis reactor', *Fuel Processing Technology*, vol. 57, no. 2, pp. 81–92.

Da Rocha Filho, G.N., Bentes, M.H.S., Brodzki, D. and Djega-Mariadassou, G. (1992) 'Catalytic conversion of Hevea brasiliensis and Virola sebifera oils to hydrocarbon fuels', *Journal of the American Oil Chemists' Society*, vol. 69, no. 3, March, pp. 266–271.

Da Rocha Filho, G.N., Brodzki, D. and Djega-Mariadassou, G. (1993) 'Formation of alkanes, alkylcycloalkanes and alkylbenzenes during the catalytic hydrocracking of vegetable oils', *Fuel*, vol. 72, no. 4, pp. 543–549.

Demirbas, A. (2007) 'The influence of temperature on the yields of compounds existing in bio-oils obtained from biomass samples via pyrolysis', *Fuel Processing Technology*, vol. 88, no. 6, June, pp. 591–597.

Demirbas, A. (2008) 'New liquid biofuels from vegetable oils via catalytic pyrolysis', *Energy, Education, Science and Technology*, vol. 21, no. 1-2, June, pp. 1–59.

Demirbas, A. (2008) 'Biodiesel: a realistic fuel alternative for Diesel engines', London: Springer.

Demirbas, A. (2009) 'Progress and recent trends in biodiesel fuels', *Energy Conversion and Management*, vol. 50, October, 14–34.

Department of Agriculture and Rural Development (DARD), (2009). *Guideline Manual for the Management of Abattoirs and other Waste of Animal Origin*, Available: www.gdard.gpg.gov.za [12 October 2015].

Department of Environmental Affairs (DEA), (2012) *National Waste Information Baseline Report*, Pretoria.

Department of Minerals and Energy (DME), (2007). *Biofuels Industrial Strategy of the Republic of South Africa*, Available: http://www.energy.gov.za/files/esources/petroleum/petroleum_bio.html#3 [17 October 2015].

Di Blasi C. (2008) 'Modeling chemical and physical processes of wood and biomass pyrolysis', *Progress in Energy and Combustion Science*, vol. 34, April, pp. 47–90.

Diepsloot, [Online], Available: http://www.joburg.org.za/index.php?option=com_content&view=article&id=7960:diepsloot-water-is-clean&catid=88:news-update&Itemid=266

Ding, J., Xia, Z. and Lu, J. (2012) 'Esterification and Deacidification of a Waste Cooking Oil (TAN 68.81 mg KOH/g) for Biodiesel Production', *Energies*, vol. 5, no. 8, July, pp. 2683-2691.

Dos Anjos, J.R.S., Gonzalez, W.D.A., Lam, Y.L. and Frety, R. (1983) 'Catalytic decomposition of vegetable oil', *Applied Catalysis*, vol. 5, no. 3, March, pp. 299–308.

Eskom (2016). *Eskom schedule of standard prices 2015/16 (Rev 00 1 April 2015)*, [Online], Available:

http://www.eskom.co.za/CustomerCare/TariffsAndCharges/WhatsNew/Documents/Eskom%20Schedule%20of%20Std%20Prices%202015_16%20excl%20Transflex.pdf [26/02/2016].

Express News Service (2015), [Online], Available: http://www.newindianexpress.com/cities/kochi/Residents-Seek-Closure-of-Abattoir/2015/04/04/article2746654.ece [12 October 2015].

Fahmi, R., Bridgwater, A.V., Donnison, I., Yates, N. and Jones, J. M. (2008) 'The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability', *Fuel*, vol. 87, no. 7, pp. 1230–1240.

Feddern, V., Cunha Junior, A., De Prá, M. C., de Abreu, P. G., Filho, J. I. d. S., Higarashi, M. M., Sulenta, M. and Coldebella, A. (2011) *Animal Fat Wastes for Biodiesel Production, Biodiesel - Feedstocks and Processing Technologies*, Dr. Margarita Stoytcheva (Ed.), China: InTech, Available: http://www.intechopen.com/books/biodiesel-feedstocksand-processing-technologies/animal-fat-wastes-for-biodiesel-production

Fonts, I., Gea, G., Azuara, M., Ábrego, J. and Arauzo, J. (2012) 'Sewage sludge pyrolysis for liquid production: A review', *Renewable and Sustainable Energy Reviews*, vol. 16, no. 5, June, pp. 2781–2805.

Gawande, M. B., Brancoa P. S. and Varma, R. S. (2013) 'Nano-magnetite (Fe_3O_4) as a support for recyclable catalysts in the development of sustainable methodologies', *Chemical Society Reviews*, vol. 42, February, pp. 3371-3393.

Gilder, A. and Mamkeli, M., *Biofuels in South Africa*, Ernst & Young. Available: www.ensafrica.com/news/biofuels-in-South-Africa?Id=1339 [15 October 2015].

Goyal, H.B., Seal, D. and Saxena, R. C. (2008) 'Bio-fuels from thermochemical conversion of renewable resources: A review', *Renewable and Sustainable Energy Reviews*, vol. 12, no. 2, February, pp. 504–517.

Grieco, E. M. and Baldi, G. (2012) '*Pyrolysis of polyethylene mixed with paper and wood: Interaction effects on tar, char and gas yields'*, Waste Management, vol. 32, no. 5, May, pp. 833–839.

Gunstone, F.D. (2001) 'Basic oleochemicals, oleochemical products and new industrial oils', in Gunstone, F.D. and Hamilton, R.J. (Eds.) *Oleochemical manufacture and applications*, Sheffield: Academic, pp. 1–22.

Guo, F., Peng, Z.G., Dai, J.Y. and Xiu, Z.L. (2010) 'Calcined sodium silicate as solid base catalyst for biodiesel production', *Fuel Processing Technology*, vol. 91, no. 3, March, pp. 322-328.

Guo, F. and Zhen, F. (2011) *Biodiesel Production with Solid Catalysts, Biodiesel - Feedstocks and Processing Technologies*, Dr. Margarita Stoytcheva (Ed.), China: InTech, Available: http://www.intechopen.com/books/biodiesel-feedstocks-and-processing-technologies/biodiesel-productionwith-solid-catalysts

Hassen-Trabelsi, A. B., Kraiem, T., Naoui, S. and Belayouni, H. (2013) 'Pyrolysis of waste animal fats in a fixed-bed reactor: Production and characterization of bio-oil and bio-char', *Waste Management*, vol. 34, October, pp. 210 – 218.

Hemalatha, K., Madhumitha, G., Kajbafvala, A., Anupama, N., Sompalle R. and Roopan, S. M. (2013) 'Function of nanocatalyst in chemistry of organic compounds revolution: An overview', *Journal of Nanomaterials* - Special issue on Self-Assembly Techniques for Nanofabrication, vol. 2013, article no. 4, January.

http://forum.hardware.fr/hfr/Discussions/Loisirs/images-etonnantes-cons-sujet_78667_2309.htm

Hughes, A. J. (2007) Fluidized Bed Reactor, [Online], Available: https://commons.wikimedia.org/wiki/File:Fluidized_Bed_Reactor_Graphic.JPG

Idem, R. O., Katikaneni, S. P. R. and Bakhshi, N. N. (1996) 'Thermal cracking of canola oil: Reaction products in the presence and absence of steam', *Energy & Fuels*, vol. 10, no. 6, pp. 1150-1162.

Inguanzo, M., Dominguez, A., Menendez, J.A., Blanco, C.G. and Pis, J.J. (2002) 'On the pyrolysis of sewage sludge: The influence of pyrolysis conditions on solid, liquid and gas fractions', *Journal of Analytical and Applied Pyrolysis*, vol. 63, no. 1, March, pp. 209–222.

International Energy Agency (IEA), (2011). *World Energy Outlook 2011*, [Online], Available: http://www.worldenergyoutlook.org/weo2011/ [19 October 2015].

Ioannidou, O., Zabaniotou, A., Antonakou, E.V., Papazisi, K.M., Lappas, A. A. and Athanassiou C. (2009) 'Investigating the potential for energy, fuel, materials and chemicals production from corn residues (cobs and stalks) by non-catalytic and catalytic pyrolysis in two reactor configurations,' *Renewable and Sustainable Energy Reviews*, vol. 13, no. 4, May, pp. 750–762.

Ito, T., Sakurai Y., Kakuta Y., Sugano M. and Hirano K. (2011) 'Biodiesel production from waste animal fats using pyrolysis method', *Fuel Processing Technology*, vol. 94, November, pp. 47 – 52.

Jahirul, M. I., Rasul, M. G., Chowdhury, A. A. and Ashwath, N. (2012) 'Biofuels production through biomass pyrolysis - A technological review', *Energies*, vol. 5, no. 12, November, pp. 4952-5001;

Jones, S.B., Holladay, J.E., Valkenburg, C., Stevens, D.J., Walton, C., Kinchin, C., Elliott, D.C., Czernik, S. (2009) '*Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case'*, U.S. Department of Energy, February.

Karan Beef, [Online], Available: http://www.karanbeef.co.za/AboutUs/Logistics [13 December 2015].

Karaosmanoglu, F., Tetik, E. and Gollu, E. (1999) 'Biofuel production using slow pyrolysis of the straw and stalk of the rapeseed plant', *Fuel Processing Technology*, vol. 59, no. 1, April, pp. 1–12.

Katikaneni, S.P.R., Adjaye, J.D. and Bakhshi, N.N. (1995a) 'Studies on the catalytic conversion of canola oil to hydrocarbons: Influence of hybrid catalysts and steam', *Energy Fuels* vol. 9, no. 4, July, pp. 599–609.

Katikaneni, S.P.R., Adjaye, J.D. and Bakhshi, N.N. (1995b). Catalytic conversion of canola oil to fuels and chemicals over various cracking catalysts. *Canadian Journal of Chemical Engineering*, vol. 73, no. 4, pp. 484–497.

Katikaneni, S.P.R., Adjaye, J.D. and Bakhshi, N.N. (1995c) 'Performance of aluminophosphate molecular sieve catalysts for the production of hydrocarbons from wood-derived and vegetable oils', *Energy Fuels*, vol. 9, no. 6, November, pp. 1065–1078.

Klass, D.L. (2004) 'Biomass for renewable energy and fuels', In: Cleveland, C.J. (Ed.), Encyclopedia of Energy, vol. 1. San Diego: Elsevier, pp. 193–212., [Online], Available: http://beraonline.org/yahoo_site_admin/assets/docs/cyclopediaofEnergy.35293015.pdf [July 15, 2015].

Konar, S.K., Boocock, D.G.B., Mao, V. and Liu, J. (1994) 'Fuels and chemicals from sewage sludge: 3. Hydrocarbon liquids from the catalytic pyrolysis of sewage sludge lipids over activated alumina', *Fuel*, vol. 73, no. 5, May, pp. 642–646.

Konwer, D., Taylor, S.E., Gordon, B.E., Otvos, J.W. and Calvin, M. (1989) 'Liquid fuels from Mesua ferrea L. seed oil', *Journal of the American Oil Chemists Society*, vol. 66, no. 2, February, pp. 223–226.

Kruger, P. (2013) Rendering Alternatives in RSA, *4th Global Feed and Food Congress*, South Africa, email to Carina (carina@soafrica.com), 15 June [21 June 2015].

Laird, D. A., Brown, R. C., Amonette, J. E. and Lehmann, J. (2009) 'Review of the pyrolysis platform for coproducing bio-oil and biochar', 169; *Biofuels, Bioproduct & Biorefining*, vol. 3, no. 5, September/October, pp. 547–562.

Lapuerta, M., Armas, O. and Rodríguez-Fernández, J. (2008) 'Effect of biodiesel fuels on diesel engine emissions', *Progress in Energy and Combustion Science*, vol. 34, no. 2, April, pp. 198-223,

Letete, T. and von Blottnitz, H. (2009) '*Biofuel Policies in South Africa: A critical analysis'*, [Online], Available: http://www.erc.uct.ac.za/Research/publications/12Letete-Blottnitz-biofuel_policies.pdf [27 October 2015].

Lima, D. G., Soares, V. C. D., Ribeiro, E. B., Carvalho, D. A., Cardoso, E. C. V., Rassi, F. C., Mundim, K. C., Rubim, J. C. and Suarez, P.A. (2004) 'Diesel-like fuel obtained by pyrolysis of vegetable oils', *Journal of Analytical and Applied Pyrolysis*, vol. 71, no. 2, June, pp. 987–996.

Long, Y. D., Guo, F., Fang, Z., Tian, X. F., Jiang, L. Q., Zhang, F. (2011) 'Production of biodiesel and lactic acid from rapeseed oil using sodium silicate as catalyst', *Bioresource Technology*, vol.102, no. 13, pp. 6884-6886.

Luo, H., Jiang, H., Klande, T., Cao, Z., Liang, F., Wang, H. and Caro, J. (2012) 'Novel cobalt-free, noble metal-free oxygen-permeable $40Pr_{0.6}Sr_{0.4}FeO_{3-\delta}$−$60Ce_{0.9}Pr_{0.1}O_{2-\delta}$ dual-phase membrane,' *Chemistry of Materials*, vol. 24, no. 11, May, pp. 2148−2154.

Luo Z., Wang S., Liao Y., Zhou, J., Gu, Y. and Cen, K. (2004) 'Research on biomass fast pyrolysis for liquid fuel', *Biomass Bioenergy*, vol. 26, no. 5, May, pp. 455–462.

Lv, P.M., Xiong, Z.H., Chang, J., Wu, C.Z., Chen, Y. and Zhu, J.X. (2004) 'An experimental study on biomass air–steam gasification in a fluidized bed', *Bioresource Technology*, vol. 95, no. 1, October, pp. 95–101.

Ma, F. and Hanna, M.A. (1999) 'Biodiesel production: A review', *Bioresource Technology*, vol. 70, no. 1, October, pp. 1–15.

Maher, K. D. and Bressler, D. C. (2007) 'Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals', *Bioresource Technology*, vol. 98, December, pp. 2351–2368.

Marcus, B.K. and Cormier, W.E. (1999) 'Going Green with Zeolites', *Chemical Engineering Progress*, vol. 95, no. 6, January, pp. 47-52.

Maschio, G., Koufopanos, C., Lucchesi, A. (1992) 'Pyrolysis, a promising route for biomass utilization', *Bioresource Technology*, vol. 42, no. 3, pp. 219–231.

McCartney, G., Hanlon, P. and Romanes, F. (2008) 'Climate change and rising energy costs will change everything: A new mindset and action plan for 21st Century public health. *Public Health*, vol. 122, issue 7, July, pp. 658-663.

Milne, T.A., Evans, R.J. and Nagle, N. (1990) 'Catalytic conversion of microalgae and vegetable-oils to premium gasoline, with shape selective zeolites', *Biomass*, vol. 21, no. 3, pp. 219–232.

Mohan, D., Pittman, C. U. and Steele, P. H. (2006) 'Pyrolysis of wood/biomass for bio-oil: A critical review', *Energy & Fuels*, vol. 20, pp. 848–889.

Muchenje, V., Nkohla, M. B., Chulayo, A. Y. and Nantapo, C. W. T. (2013) Abattoir Environmental Health, [Online], Available: http://www.ehrn.co.za/lectureseries/index.php [21 October 2015]

National Biodiesel Board (NBB), (2005). Biodiesel Backgrounder Factsheet, [Online], Available: http://biodiesel.org/what-is-biodiesel/biodiesel-fact-sheets [October 30, 2015].

Neethling, G. (2014) *Waste Management: Red Meat Abattoirs*, [Online], Available: . http://www.wasteroadmap.co.za/download/ims2014_present09.pdf [15 September 2015].

NETL, National Energy Technology Laboratory, Available: http://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/fixed-bed-reactor

Oasmaa A. and Czernik S. (1999) 'Fuel oil quality of biomass pyrolysis oils - State of the art for the end users', *Energy & Fuels*, vol. 13, no. 3, pp. 914–921.

Oasmaa A. and Peacocke, G.V.C. (2010) *Properties and fuel use of biomass-derived fast pyrolysis liquids. A guide*, VTT Technical Research Centre of Finland, Finland: VTT Publications, vol. 731.

Onay, O. and Kockar, O.M. (2004) 'Fixed bed pyrolysis of rapeseed (Brassica napus L)', *Biomass Bioenergy*, vol. 26, pp. 289 – 299.

Ozcimen, D. and Karaosmanoglu, F. (2004) 'Production and characterization of bio-oil and biochar from rapeseed cake', *Renewable Energy*, vol. 29, no. 5, April, pp. 779–87.

Pinto, A.C., Guarieiro, L. L. N., Rezende, M.J.C., Ribeiro, N. M., Torres, E. A., Lopes, W. A., Pereira, P. A. and Andrade, J. B. (2005) 'Biodiesel: An overview', *Journal of the Brazil Chemical Society*, vol. 16, no. 6b, pp. 1313–1330.

Putun, E., Uzun B.B. and Putun A.E. (2009). 'Rapid pyrolysis of olive residue. 2. Effect of catalytic upgrading of pyrolysis vapors in a two-stage fixed-bed reactor', *Energy & Fuels*, vol. 23, pp. 2248-2258.

Qi, Z., Jie, C., Wang, T. and Yung, X. (2006) 'Review of Biomass Pyrolysis Oil Properties and Upgrading Research', *Energy Conversion and Management*, vol. 48, June, pp. 87-92

Rao, M.S., Singh, S.P., Sodha, M.S., Dubey, A.K. and Shyam, M. (2004) 'Stoichiometric, mass, energy and exergy balance analysis of countercurrent fixed-bed gasification of post-consumer residues', *Biomass and Bioenergy*, vol. 27, no. 2, August, pp. 155–171.

Sang, O.Y., Twaiq, F., Zakaria, R., Mohamed, A.R. and Bhatia, S. (2003) 'Biofuel production from catalytic cracking of palm oil', *Energy Sources*, vol. 25, no 9, pp. 859–869.

Scahill, J., Diebold, J.P. and Feik, C. (1996) *Removal of residual char fines from pyrolysis vapors by hot filtration*, [Online], Available: http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.387.9448&rep=rep1&type=pdf [30 August 2015].

Schuchardt, U., Sercheli, R., and Vargas, R.M. (1998) 'Transesterification of vegetable oils: A review', *Journal of the Brazilian Chemical Society*, vol. 9, no. 3, May, pp. 199–210.

Scott, D.S. and Piskorz, J. (1984) 'The Continuous Flash Pyrolysis of Biomass', *The Canadian Journal of Chemical Engineering*, vol. 62, no. 3, pp. 404-412.

Shihadeh, A. and Hochgreb, S. (2002) 'Impact of biomass pyrolysis oil process conditions on ignition delay in compression ignition engines,' *Energy & Fuels*, vol. 16, no. 3, pp. 552–561.

Shrestha, D. and Gerpen, J. V. (2010) 'Biodiesel from Oilseed Crops', in Singh, B.P. (Ed.) *Industrial Crops and Uses*, Wallingford: CABI, pp. 140-156.

Singh, S.B. and Tandon, P.K. (2014) 'Catalysis: A brief review on nano-catalyst', *Journal of Energy and Chemical Engineering*, vol. 2, no. 3, pp. 106-115.

Sipila, K., Kuoppala, E., Fagernas, L. and Oasmaa, A. (1998) 'Characterization of biomass–based flash pyrolysis oils', *Biomass and Bioenergy*, vol. 14, no. 2, pp. 103–113.

South Africa - Electric power transmission and distribution losses, [Online], Available: www.indexmundi.com/facts/south-africa/electric-power-transmission-and-distribution-losses [7 March 2016].

South Africa info (2006) *IDC boosts SA's biofuel industry*, 13 March 2006, Available: http://www.southafrica.info/business/trends/newbusiness/biofuels-idc.htm#.VWg2fU0w_IU [29 May 2017]

South Africa info, (2013) SA to blend biofuels from 2015, 1 October 2013, Available: www.southafrica.info/business/trends/newbusiness/biofuels-011013.htm [29 May 2017]

South African Petroleum Industry Association (SAPIA), (2008) *Petrol and diesel in South Africa and the impact on air quality*. [Online], Available: http://www.sapia.org.za/Publications [12 November 2015].

Srivastava, A. and Prasad, R. (2000) 'Triglycerides-based diesel fuels', *Renewable and Sustainable Energy Reviews*, vol. 4, no. 2, June, pp. 111–113.

Stern, N. (2008) 'The economics of climate change', *American Economic Review*, vol. 98, no. 2, May, pp. 1-37.

Tans, P. and Keeling, R. (2011) 'Trends in atmospheric carbon dioxide, [Online], Available: http://www.esrl.noaa.gov/gmd/ccgg/trends/ [12 September 2015]

Twaiq, F.A., Zabidi, N.A.M., and Bhatia, S. (1999) 'Catalytic conversion of palm oil to hydrocarbons: Performance of various zeolite catalysts', *Industrial and Engineering Chemistry Research*, vol. 38, no. 9, August, pp. 3230–3237.

United Nations Environment Programme (UNEP), (2013). *Methodological guide for the development of inventories of hazardous wastes and other wastes under the Basel Convention*, Series/SBC No: 99/009 (E) Geneva, October, [Online], Available: http://www.basel.int/Implementation/LegalMatters/Compliance/GeneralIssuesActivities/Activities201415/Guidanceoninventories/tabid/3560/ctl/Download/mid/11291/Default.aspx?id=1&ObjID=7831. [26 May 2015].

U.S. Energy Information Administration (EIA), (2011). *Annual Energy Outlook 2011*, Center for Strategic and International Studies. Available: http://www.eia.gov/pressroom/presentations/howard_09192011.pdf [25 June 2015].

United States Department of Agriculture (USDA), (2010). *Foreign Agricultural Service*, [Online], Available: http://www.fas.usda.gov/psdonline/ [18 March 2010].

Vonghia, E., Boocock, D.G.B., Konar, S.K. and Leung, A. (1995) 'Pathways for the deoxygenation of triglycerides to aliphatic hydrocarbons over activated alumina', *Energy & Fuels*, vol. 9, no. 6, November, pp. 1090–1096.

Wang, X., Kersten, S.R.A., Prins, W. and van Swaaij, W.P.M. (2005) 'Biomass pyrolysis in a fluidized bed reactor. Part 2: Experimental validation of model results, *Industrial & Engineering Chemistry Research*, vol. 44, no. 23, October, pp. 8786–8795.

Water Research Commission (WRC), '*Research into the purification of abattoir effluent by means of a protein recovery process*', [Online], Available: http://www.wrc.org.za/Lists/Knowledge%20Hub%20Items/Attachments/8002/KV-166-05_FOREWORD.pdf [4 June 2015].

Weitkamp, J. (2000) 'Zeolites and catalysis', *Solid State Ionics*, vol. 131, pp. 175–188.

What is Pyrolysis? [Online], Available: http://www.pyrolysisplant.com/what-is-pyrolysis/ [June 10, 2015].

Wiggers, V.R., Wisniewski Jr., A., Madureira, L.A.S., Chivanga Barros, A.A. and Meier, H.F. (2009) 'Biofuels from waste fish oil pyrolysis: Continuous production in a pilot plant', *Fuel*, vol. 88, no. 11, November, pp. 2135–2141.

Wisniewski Jr., A., Wiggers, V.R., Simionatto, E.L., Meier, H.F., Barros, A.A.C. and Madureira, L.A.S. (2010) 'Biofuel from waste oil pyrolysis: Chemical composition', *Fuel*, vol. 89, pp. 563–568.

World Bank (2013). *Toward a Sustainable Energy Future For All: Directions for the World Bank Group Energy Sector*. Geneva, Switzerland. [Online], Available: http://www.wds.worldbank.org [30 May 2015]

World Bank Study (2008) '*Conditions at Slaughterhouses'*, Livestock and Slaughter Waste Management, February.

Yaman, S. (2004) 'Pyrolysis of biomass to produce fuels and chemical feedstocks', *Energy Conversion and Management*, vol. 45, pp. 651–671

Zaher, F.A. and Taman, A.R. (1993) 'Thermally decomposed cottonseed oil as a diesel engine fuel', *Energy Sources*, vol. 15, no. 3, July, pp. 499–504.

Zanzi, R., Sjostrom, K. and Bjornbom, E. (1996) 'Rapid high-temperature pyrolysis of biomass in a free-fall reactor', *Fuel*, vol. 75, no. 5, April, pp. 545–550.

APPENDIX I

RESEARCH OUTPUT

Bio Diesel Conference

- **Conference Title**: Bio Diesel for a Greener Economy – Progress, Obstacles & Opportunities
- **Participation**: Speaker
- **Presentation Title**: Biofuel As An Alternative Fuel
- **Organiser**: Southern African Bioenergy Association
- **Date**: 20 November 2015
- **Venue**: Midrand, South Africa

APPENDIX II

BASIC OPERATION / PROGRAMMING
EUROTHERM 2216 PID CONTROLLER

Use as a PID Setpoint Controller.

Press either the 'UP' ▲ or 'DOWN' ▼ buttons to adjust the lower displayed reading to indicate the required setpoint. The furnace will heat up at its fastest rate to the setpoint once the furnace door is closed and the 'HEAT ON' switch is moved to the (1) position.

To avoid damage to the load or furnace refractories, it is desirable to limit the rate of temperature rise.

The 2216 controller has a facility enabling a ramp rate to be set so that, when enabled, the rate of rise or fall in temperature (depending on the setpoint relative to the actual furnace temperature), can be closely controlled.

Access to this parameter setting is achieved by pressing the scroll (second from left) button 2 times until "SPrr" is indicated. The bottom display will show "OFF" as per factory setting. To set the required rate of temperature rise i.e., °C per minute, press the up ♦ button to cause the button display to read the desired figure.

When this parameter has been set, the ramp facility will remain enabled until the setting for "SPrr" has been returned to "OFF".

Self Tuning

This facility enables automatic adjustment of the P.I.D. control terms. For a full description of this, consult the enclosed booklet. To access this facility, press the "PAGE" (left hand side) button twice until "Atun" shows on the top display. "TunE OFF" will be displayed on the lower display.

To enable autotune, push the UP ▲ button to change the bottom display to "ON".

Autotune cannot be started when the ramp to setpoint "SPrr" is in use.