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Catalytic conversion of alcohol-waste vegetable oil mixtures over aluminosilicate catalysts

A thesis submitted towards the fulfilment of the requirements for the degree of

Master of Engineering: Chemical Engineering

Elvis Tinashe Ganda

Supervisor: Dr. Yusuf Isa, Makarfi

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Declaration

I hereby declare that the content of this thesis is a record of my original research work towards achieving the Master of Engineering in Chemical Engineering at the Durban University of Technology (DUT). The content of this research document has not been previously published or written by another person for the award of any other degree at DUT or in any other educational institution. Furthermore, I declare that the content of this thesis does not violate any copyright as every work of others has been indicated and recognized by means of in text referencing and comprehensive list of references.

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Elvis Tinashe Ganda

Signature:………………………………………..Date:…………………..

Supervisor: Dr. Yusuf Isa, Makarfi

Signature:………………………………………..Date:………………………

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Publications

Isa, Yusuf Makarfi and Elvis Tinashe Ganda. "Bio-oil as a potential source of petroleum range fuels." *Renewable and Sustainable Energy Reviews* 81 (2018): 69-75.

Abstract

Thermochemical catalytic conversion of ethanol-waste cooking oil (eth-WCO) mixtures was studied over synthesised aluminosilicate catalysts HZSM-5, FeHZSM-5 and NiHZSM-5. The thermochemical reactions were carried out at temperatures of 400° and 450°C at a fixed weight hourly space velocity of 2.5 h^{-1} in a fixed bed reactor system. Successful conversion of the eth-WCO mixtures was carried out over the synthesised catalyst systems and in order to fully understand the influence of the catalysts, several techniques were used to characterise the synthesised materials which include XRD, SEM, EDS, BET techniques.

Results of the catalyst characterisation showed that highly crystalline solid material had been formed as evidenced by the high relative crystallinity in comparison with the commercial HZSM-5 catalyst at 2θ peak values of 7°- 9° and 23°- 24°. The introduction of metals decreased the intensity of the peaks leading to lower values of relative crystallinity of 88% and 90% for FeHZSM-5 and NiHZSM-5, respectively. However this was even slightly higher than the commercial sample which had a value of 86% with respect to HZSM-5 synthesised catalyst taken as reference material. There was no significant change in XRD patterns due to the introduction of metal. Elemental analysis done with energy dispersive spectroscopy showed the presence of the metal promoters (Fe, Ni) and the Si/Al ratio obtained from this technique was 38 compared to the target ratio of 50 set out initially in the synthesis. From the SEM micrographs the morphology of the crystals could be described as regular agglomerated sheet like material. Surface area analysis showed that highly microporous crystals had been synthesised with lower external surface area values ranging from 57.23 m^2/g - 100.82 m^2/g compared to the microporous surface area values ranging from 195.96 m^2/g to 212.51 m^2/g.

For all catalyst employed in this study high conversions were observed with values of over 93 %, almost total conversion was achieved for some samples with values as high as 99.6 % with FeHZSM-5 catalysts. Despite the high level of conversion the extent of deoxygenation varied with lower values recorded for FeHZSM-5 (25%WCO) at 400°C and NiHZSM-5

(75%WCO) at 450°C with oxygenated hydrocarbons of 19.5% and 19.33% respectively. The organic liquid product yield comprised mostly of aromatic hydrocarbon (toluene, p-xylene and naphthalene) decreased with the introduction of metal promoters with NiHZSM-5 producing higher yields than FeHZSM-5. For the pure waste cooking oil (WCO) feedstock the parent catalyst HZSM-5 had a liquid yield of 50% followed by NiHZSM-5 with 44% and lastly FeHZSM-5 had 40% at 400°C which may be seen to follow the pattern of loss of relative crystallinity.

An increase in operating temperature to 450°C lowered the quantity of organic liquid product obtained in the same manner with the HZSM-5 parent catalyst still having the highest yield of 38% followed by Ni-HZSM-5 with 36% and Fe-HZSM-5 having a value of 30% for pure waste cooking oil feedstock which may be attributed to thermally induced secondary cracking reactions. For all catalyst systems with an increase in the content of waste cooking oil from 25% to 100% in the feed mixture there was a linearly increasing trend of the liquid product yield. HZSM-5 catalyst increased from 14% to 50% while FeHZSM-5 increased from 16% to 40% and NiHZSM-5 increased from 12% to 44% at a temperature setting of 400°C with lower values observed at 450°C.Results obtained in this study show the potential of producing aromatics for fuel and chemical use with highly microporous zeolite from waste material such as waste cooking oil forming part of the feedstock.

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Acronyms

WCO	Waste cooking oil
Eth-WCO	Ethanol-waste cooking mixture
OLP	Organic liquid product
IEA	International energy agency
GHG	Greenhouse gas
CO_e	Carbon dioxide equivalence
CO_2	Carbon dioxide gas
COP	Conference of parties
PET	Polyethylene terephthalate
ZSM-5	Zeolite Socony Mobil-5
BTEX	Benzene, toluene, ethylbenzene, xylene
EDS	Energy dispersive x-ray spectroscopy
SEM	Scanning electron microscope
XRD	X-ray diffraction
BET	Brunauer–Emmett–Teller

Chapter 1

1.1 Introduction and Background

Production of fuel and chemical feedstock from carbon neutral sources such as biomass has become an area of increased interest as the drive towards a low carbon society and economy intensifies (Huber and Corma 2007); Kadrmas *et al.* (2015); (Ennaert *et al.* 2016; Wiggers *et al.* 2017). It is recognised that the development of alternative, cleaner sources of fuels and chemicals from biomass can increase energy security and address environmental concerns (Iliopoulou *et al.* 2012; Karatzos *et al.* 2014; Ennaert *et al.* 2016). Biofuels have the potential to lower the environmental carbon footprint with the renewable nature of feedstock theoretically making peak supply concerns disappear, in contrast to the finite nature of fossil fuels (Huber and Corma 2007; Rye *et al.* 2010; Ennaert *et al.* 2016). Despite the potential of biofuels, feedstock production systems for biomass could stretch natural resources such as land and water in order to contribute significantly to the increased demand for transportation fuel (Bessou *et al.* 2011; Bhargava 2011).

Issues have been raised about the potential negative effects of increased agricultural activities to support the biofuel sector; thus research development and deployment of biofuels should seek sustainable feedstock utilisation (National Academy of Sciences *et al.* 2009; Hassan *et al.* 2015; Xu *et al.* 2016). Cellulosic feedstock, inedible oils have been sought in this regard to allow for sustainable technology development, while simultaneously targeting reduced greenhouse gas (GHG) emissions to slow down climate change which will threaten our very existence and survival if not dealt with urgently (Huber and Corma 2007; Bessou *et al.* 2011; Dutta *et al.* 2014; Xu *et al.* 2016). The increased consumption of edible oil has led to increased rate of waste cooking oil production from households and fast food outlets (Talebian-Kiakalaieh *et al.* 2013; Yaakob *et al.* 2013; Kurnia *et al.* 2016). Though regulations are available on the proper disposal of waste cooking oil, there is fear that some of the streams are finding their way to waste water treatment plants complicating the treatment processes (Talebian-Kiakalaieh *et al.* 2013; Yaakob *et al.* 2013; Kurnia *et al.*

2016). Waste cooking oil has the potential to be used as a feedstocks for the production of fuels and chemicals nullifying its status as a waste pollutant to the environment (Talebian-Kiakalaieh *et al.* 2013). In this study, the catalytic conversion of ethanol and waste cooking oil mixtures were investigated using three synthesised catalysts.

Although fossil fuels will continue to be a critical source of transportation fuel and material for the petrochemical industry in the medium term; their finite, non-renewable nature and contributions to global warming has prompted a search for sustainable alternatives (Chew and Bhatia 2008; Cherubini 2010; Galadima and Muraza 2015a). The increased greenhouse gas (GHG) emission released from the extensive use of fossils has to be curbed before catastrophic damage is done (Cherubini 2010). Greenhouse gas emission has caused an increase in the global average temperature with the rise now pegged at over 1 °C and on the backdrop of the COP21 Paris conference, a 2 °C cap by 2050 was set to limit damage to the ecosystem and environment (Clémençon 2016). Expectations are the Paris deal will see increased divestment from a highly fossil fuel oriented society to a renewable based society (Clémençon 2016).

The scientific evidence on global warming is alarming, and this has forced the world to take notice and push for action as evidenced by the signing of the Paris accord of 2015. The agreement will see the global community strive towards keeping the average rise in global temperature to below 2 °C as per pre industrial time levels (Clémençon 2016) . However, this target is easier said than done, as there has been continued increase in GHG emission which has contributed immensely to the warming effect with CO_2 emission from fossil fuel usage at very high levels compared to industrial levels (Clémençon 2016). The Paris agreement is built entirely on voluntary pledges to decarbonise the economies thus reduce the emission contribution to the atmosphere unlike previous treaties (Kyoto protocol based on differential responsibilities) which looked at redressing the imbalance caused from historic contributions to the atmosphere (Clémençon 2016). There is a feeling that developed nations have been let off the hook with their historic emissions having led the global community to this point where action needs to be taken urgently to avoid catastrophic impacts from the continued warming as a result of GHG emissions (Clémençon 2016). One of the key pillars of the Paris agreement hopes that in the near future a balance is found between anthropogenic emissions by sources and removals by sinks is achieved.

Significant uncertainties on how long petroleum reserves will last exist, price volatility of crude oil has seen the growth of the bioenergy sector (Popp *et al.* 2014; Hassan *et al.* 2015). Geopolitical landscape will continue to play a key role in policy shift towards low carbon economies (Hassan *et al.* 2015). However, climate change is a global problem requiring a holistic global approach through ramping up mitigation efforts. Major headway based on well-developed state of the art technology has seen the power (electricity) sector decarbonising its operations through investment in nuclear, wind, solar and hydro energy schemes (Cherubini 2010; Hassan *et al.* 2015). The transport system’s heavy dependence on energy dense liquid fuels has indebted them to fossil resources in the form of petroleum and natural gas (Cherubini 2010; Lemoine 2013; Hassan *et al.* 2015; Kurnia *et al.* 2016) as feedstock for the production of the various classes of hydrocarbons useful as fuels for the road, air and marine transport systems.

The transport sector is responsible for about a quarter of global carbon emissions as shown in Figure 1 which have been said to be major drivers of climate change (Hassan *et al.* 2015; Kurnia *et al.* 2016). Biomass has emerged as a promising starting block for alternative fuel and chemical production as the drive towards cleaner energy systems intensifies (Demirbas 2009; Cherubini 2010; Demirbas 2011; Popp *et al.* 2014).The growth of biomass based refineries has been founded on the wide distribution, abundance and renewable nature of these resource on a global scale (Bessou *et al.* 2011; Lemoine 2013). Biofuel, a product of biomass refinery operations, offers a possible route for the mitigation of the net GHG emissions as the CO_2 emitted upon fuel combustion, can be sequestered from the atmosphere during the biomass growth with lower emission profiles compared to its petroleum refinery counterparts (Bessou *et al.* 2011; Hassan *et al.* 2015; Kordulis *et al.* 2016).

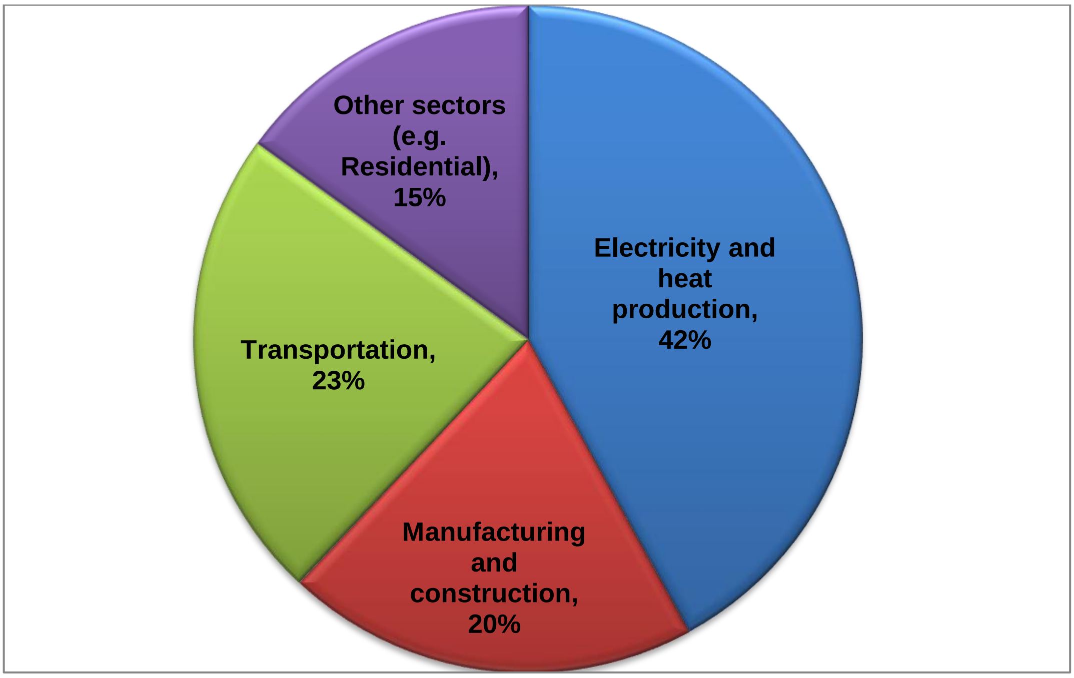

Figure 1, Global carbon emissions by sector, Source: British Petroleum Company (2014)

Crude oil has been the primary source of transportation fuels since the early 20th century (1900s) due to its favourable energy density, ease of distribution, and abundance (National Academy of Sciences *et al.* 2009; Lemoine 2013). Currently fossil resource supply more than 80% of global energy needs (Karatzos *et al.* 2014; Popp *et al.* 2014; Hassan *et al.* 2015) The growing demand and use of fossil fuel has led to increasing greenhouse gas emissions (Popp *et al.* 2014; Hassan *et al.* 2015). Although the development of biofuels has shown steady growth in recent years, they still only represent around 3% of global transport fuel consumption (Karatzos *et al.* 2014; Xu *et al.* 2016).

The greatest challenge for the 21st century is to decouple economic growth and social development from increasing GHG emissions which are threating the environment through climate change (Popp *et al.* 2014; Hassan *et al.* 2015; Emori *et al.* 2016). With an increase in carbon emissions from fossil fuel use, one of the most valuable carbon sink to counteract the high emission is continuously being lost due to increased land-use change resulting in the clearing of forests and vegetation (Cherubini 2010; Bessou *et al.* 2011). Minimal or total avoidance of land-use change need to be practised in the transition to low carbon economies especially with respect to production of biofuel feedstock (Cherubini 2010; Bessou *et al.* 2011). Another aspect to consider is the minimal usage of fossil fuel resource in the conversion pathway in order to realise better net GHG savings (Cherubini 2010; Bessou *et al.* 2011).

1.2 Biomass and biofuels

Numerous technologies have been developed to convert biomass to transport fuels, chemical feedstock and energy (Huber and Corma 2007; Khan 2011; Islam *et al.* 2012). Biofuel production routes that have been commercialised successfully are utilising food crops (starch, sugar and oil seed crops) as feedstock (Huber and Corma 2007; Jae *et al.* 2011; Khan 2011). The use of food crops for fuel has been met with mixed feelings, with some critics fearing the practise will drive up food prices as well as put pressure on natural resources such as land and water (Huber and Corma 2007; Khan 2011). Some argue that there is extraordinary space to accommodate all farming systems to cater for biofuel and food without compromising food security and the balance of the ecosystem (Dupont *et al.* 2009; Bessou *et al.* 2011; Emori *et al.* 2016). However, Africa with the vast area of arable land is plagued with underutilisation and lack of practise in modern farming methods to sustain the emerging bio-sector (Amigun *et al.* 2011; Pradhan and Mbohwa 2014). The assumption that crop based biofuels offer a lower carbon footprint (GHG reduction) relative to petroleum fuels has been a source of conflict, with suggestions pointing to the need for a comprehensive cradle to grave life cycle assessment (LCA) (Dupont *et al.* 2009; Cherubini 2010; Bessou *et al.* 2011; Kurnia *et al.* 2016).

Thermochemical approaches hold great promise for biomass conversion to liquid biofuel with triglyceride feedstock conversion through transesterification, catalytic cracking, pyrolysis and hydro treatment having been explored (Huber and Corma 2007; Khan 2011; Islam *et al.* 2012). “Drop-in alternatives” can be defined as bio-hydrocarbons that are functionally equivalent to petroleum fuels and chemical precursors while fully compatible with existing infrastructure and processes (Khan 2011; Islam *et al.* 2012; Karatzos *et al.* 2014). Product similarity with fossil fuels of thermochemical transformation of biomass feedstock via cracking (thermal or catalytic) has allowed for increased attractiveness in usage and development of drop-in alternatives (French and Czernik 2010; Khan 2011; Karatzos *et al.* 2014). The use of electric vehicles has been explored, however the projections show that internal combustion engines will continue to be extensively used thus there will always be a need for carbon based fuels (Huber and Corma 2007; Karatzos *et al.* 2014). The drop-in alternatives should be able to serve the needs of internal combustion engines in the event that electric transportation systems increase in adoption and use(Khan 2011).

The use of aluminosilicate catalysts in the upgrading process of oxygenated hydrocarbons have been explored taking cues from the commercial success of the methanol to gasoline (MTG) process that was based on successful utilisation of zeolites (French and Czernik 2010). The MFI structured zeolites in the form of ZSM-5 which are aluminosilicates proved most efficient producing high octane rated fuels with a selectivity leaning towards the gasoline range hydrocarbons (Chen *et al.* 2010; French and Czernik 2010; Galadima and Muraza 2015a, 2015b). The success of this venture opened room for research and development into the use of biomass derived alcohols as feedstock for fuel and chemical feedstock production (French and Czernik 2010; Galadima and Muraza 2015b). However, the high water content of fermentation broth has been known to result in faster deactivation of zeolite catalyst and several works have explored the synthesis versatility zeolites in order to upgrade alcohols (Galadima and Muraza 2015b). The increased need to lower greenhouse emissions and limitations on the use of 1st generation biofuels has allowed for increased scrutiny into ways of upgrading biomass derived feedstock (Huber and Corma 2007; Khan 2011). The use of the ZSM-5 zeolite has been explored in this regard due its nature that allows for modification and tailored synthesis to influence activity and selectivity (Galadima and Muraza 2015b; Hassan *et al.* 2015). The current study has been premised upon the need to produce drop-in biofuels and chemical feedstock from an integrated feedstock of ethanol and waste cooking oil a potential waste with disposal issues if not handled properly.

1.3 Problem statement

Research has shown that part of the waste cooking oil is underutilised ending up in wastewater treatment plants which is not ideal for the environment, and a loss to society as its carbon content could contribute to lowering stress on conventional carbon sources if valorised to fuels and chemicals (Khan 2011; Islam *et al.* 2012). The synthesis and integration of aluminosilicate catalysts to biomass derived feedstock valorisation has been receiving increased interest in research and development in order to create analogous refinery operations based on biomass feedstock (Huber and Corma 2007; Khan 2011). Tailoring catalyst to upgrade biomass derived feedstock will allow for the production of drop-in alternatives to augment the current petroleum derived products ranging from fuel and petroleum feedstock (Khan 2011; Karatzos *et al.* 2014). The unique qualitative feature that makes biomass derived feedstock processing difficult is their relative lower effective hydrogen index as a result of the oxygen content (Jae *et al.* 2011; Karatzos *et al.* 2014). The processing of feedstock with lower effective hydrogen index with zeolites done to date has been characterised with high production of gases and coke (Jae *et al.* 2011; Karatzos *et al.* 2014). Successful tailoring of catalyst to improve the effective hydrogen index in the absence of external hydrogen source is an interesting option being explored with feedstock such as bio-oils, ethanol and triglycerides (Jae *et al.* 2011; Khan 2011). Integrated processing of the liquid renewable feedstocks mentioned above could be explored in a manner similar to the processing of crude oil in refineries (Huber and Corma 2007; Khan 2011). This project aims to synthesise three catalysts and use them to convert ethanol and cooking oil waste mixtures into biofuels.

1.4 Aims and Objectives

The research project considered successful synthesis and modification of zeolite ZSM-5 catalyst for use in the conversion of ethanol-waste cooking oil mixtures to fuel range hydrocarbons.

The following objectives were useful to achieve the purpose of the study;

- preparation of ZSM-5 zeolite catalyst for the conversion of ethanol-waste cooking oil to fuel range hydrocarbons,
- investigation of the effect of feed composition on product distribution,
- investigation of the effect of temperature on liquid organic yield selectivity,
- investigation of the effect of catalyst properties on product distribution,

1.5 Scope of research

The scope of this study will focus on two major areas, the first one being the development and physical characterisation of aluminosilicate catalysts with the target group being the zeolite ZSM-5 family. The solid catalysts from the preparation stage were characterised using different analytical methods to ascertain their structure, morphology, and surface area. The second part is on the test activity of the catalysts developed with analysis to focus on the organic liquid product from the conversion of ethanol-waste cooking oil mixtures. The work focused mainly on characterisation of liquid products while the gaseous ones were quantitatively analysed.

1.6 Structures of thesis

The thesis is made up of the following sections to discuss the work done on the conversion of ethanol-waste cooking oil mixtures over synthesised aluminosilicate catalyst systems. Before the introductory chapter, summarised results are highlighted in the abstract presented.

Chapter 1

The introduction looks at possible ways to increase development and implementation renewable based economies producing fuels and chemicals sustainably to lower the environmental footprint associated with human activities. Catalytic upgrading has been proposed as a means to improve biomass based feedstock characteristics to meet societal demands in term of fuels and chemicals.

Chapter 2

In this section literature is reviewed on fossil oriented economies successes and problems, as well as how biomass derivable feedstocks may augment future outputs in terms of fuel and chemical supply. The role of aluminosilicate in the form of zeolite ZSM-5 in the thermochemical processing is discussed with particular emphasis on the thermo-catalytic upgrade of biomass material in the form of triglycerides and alcohols.

Chapter 3

This section focuses on the experimental procedure done on the thermochemical upgrade of the ethanol-waste cooking oil mixtures with two major sections; catalyst preparation and characterisation and test activity to check the influence of the synthesised catalyst.

Chapter 4

Results and discussions of the successful synthesis of the ZSM-5 catalyst and test activity study are presented

Chapter 5

This is the section dedicated to conclusions summary and recommendations derived from the current study.

In the section of references all literature sources consulted over the course of the work are presented. The last section of the thesis contains the appendix with important data is presented in table form with results from the catalysts testing presented. At the end of the appendix section the publication accepted during the course of this work has been placed.

Chapter 2

2.1 World energy dilemma

Fossil fuels remain mankind largest source of energy (Huber and Corma 2007; Hassan *et al.* 2015). These resources have been formed by exposure over millions of years of the fossilised remains of dead plants and animal organisms buried in the earth (Bessou *et al.* 2011; Islam *et al.* 2012). After taking millions of years to create, fossil resources are depleting at a faster rate than they can be replenished on a human timescale as well as contributing to the rising emission levels for GHG responsible for climate change and environmental degradation (Bessou *et al.* 2011; Islam *et al.* 2012). Modern society is extremely susceptible to economic disruptions emanating from fossil fuel markets (Huber and Corma 2007). There is fear that as the resource continues to deplete extraction and processing cost will increase, transferable to consumers leading to increased cost of electricity and transportation (Hassan *et al.* 2015). The disruptive economic and environmental factors mentioned above have driven the evolution of the biofuel industry (Huber and Corma 2007). Fossil fuels have enjoyed a century's worth of investment, research and development and the same has to happen to emerging biomass conversion technologies to make it competitive and sustainable (Huber and Corma 2007; Bessou *et al.* 2011; Khan 2011).

Fears over energy security as global peak production predictions fast approach, along with fluctuating prices and pollution problems associated with petroleum based sources have increased the urgency to find alternatives (Bessou *et al.* 2011; Kurnia *et al.* 2016). Diversification of supply will allow for liberation from the over-reliance on petroleum derived fuels, improving energy security and playing a key role in environmental protection (Huber and Corma 2007; Khan 2011; Hassan *et al.* 2015). Depending heavily on foreign crude oil imports for many non-oil producers have put economies under stress from huge import bill and supply disruptions (Huber and Corma 2007; Vanderschuren *et al.* 2008). The industrial revolution brought about high levels of economic growth and standard of living and with it a high dependence on modern forms of energy which saw the use of traditional biomass energy reduced (Huber and Corma 2007; Bessou *et al.* 2011; Khan 2011). This positive development was coupled with significant growth in carbon emissions into the atmosphere (Huber and Corma 2007). A holistic approach from developed and developing nations is required to significantly cut emissions thus prevent catastrophic effect from the continued warming of the planet and change in weather patterns (Islam *et al.* 2012).

One of the major contributors to the GHG emissions is the transportation sector which contributes about a quarter of the gas emissions (Khan 2011; Hassan *et al.* 2015). Close to 95% of the current transportation needs are met by crude oil with road transport, in particular private vehicle make the greatest contribution to the GHG emissions from this sector (Hassan *et al.* 2015). To reduce transport related GHG emissions, low carbon fuels (i.e. fuels that generate significantly less trapping gas per unit energy delivered in contrast to petroleum derivatives) will need to be employed (Bessou *et al.* 2011; Hassan *et al.* 2015). Biofuels offer great potential to reduce transport related emissions with ease of integration to existing infrastructure while promoting economic growth and energy security with less dependence on foreign oils (Cherubini 2010; Bessou *et al.* 2011). The illustration in Figure 2 shows the fuel type demand patterns for the transportation sector with the internal combustion engines run on diesel and petrol expected to continue to be major consumers of fossil fuels. With Figure 2 showing a projected high dependence on petrol and diesel run fuels, alternative drop-in biofuel use should present minimal disruptions to the transportation sector requiring little or no engine redesign and modification if the characteristics of the fuel match those derived from fossil resources (Jae *et al.* 2011; Karatzos *et al.* 2014).

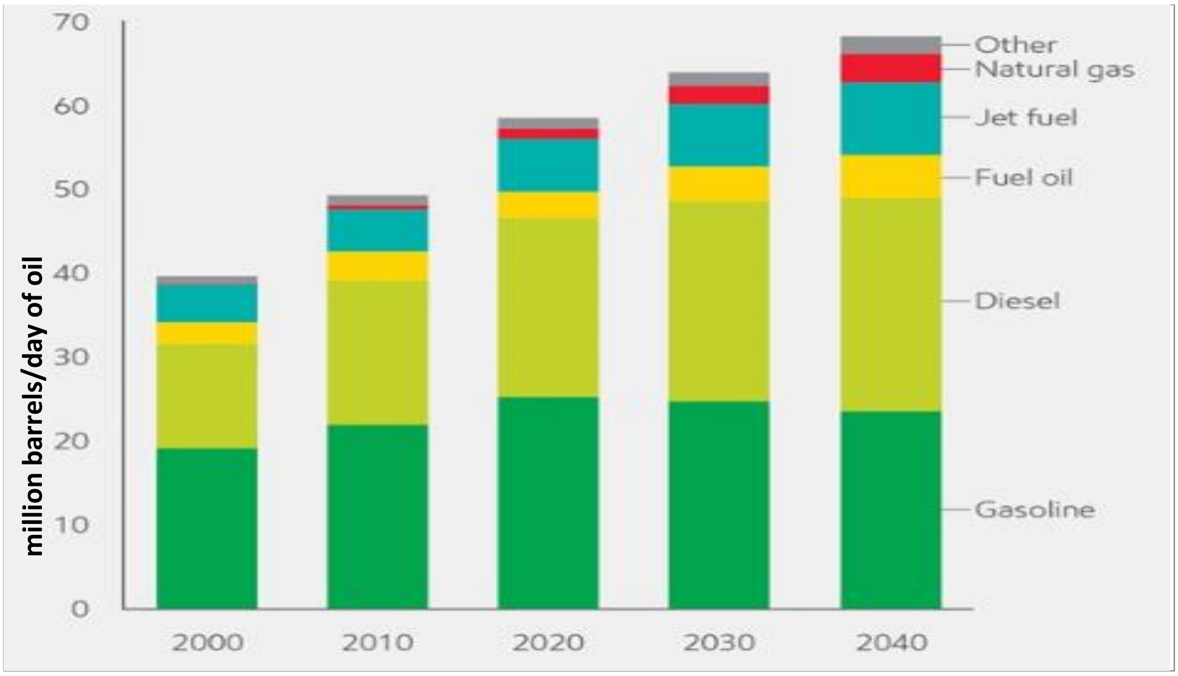

Figure 2, Global transportation energy demand by fuel type, Source: Exxon Mobil (2017)

The rate at which human economies and societies are emitting the GHG's far exceeds the capacity of natural ecosystems to sequester (reabsorb) (Bessou *et al.* 2011; Islam *et al.* 2012). Forest clearing and unsustainable agricultural practises are reducing the earth's natural ability to absorb GHG's (Islam *et al.* 2012). Although it has been acknowledged that Africa has contributed least to GHG concentration, it faces the worst consequences and has the least capacity to cope with climate change impacts (Vanderschuren *et al.* 2008; Prasad 2010; Pradhan and Mbohwa 2014). Developing countries are vulnerable to the impact of climate change and a transition to a climate resilient and lower carbon economy and society is critical to the drive towards sustainable economic and social growth (Vanderschuren *et al.* 2008; Prasad 2010; Pradhan and Mbohwa 2014). There is need to contribute to the global effort to stabilise GHG concentration to avoid dangerous anthropogenic interference with the climate system in a sustainable manner (Bessou *et al.* 2011; Islam *et al.* 2012). Global warming which is an increase in the average rise of the temperature of the earth's surface has resulted in global climate change (Islam *et al.* 2012). The rise in average global temperature has primarily being as a result of increased GHG concentration emitted through human activities with the gases contributing to a natural phenomenon called greenhouse effect (Bessou *et al.* 2011; Emori *et al.* 2016).

Crops generating starch, sugars and/ oil are the major sources of feed for alternative fuel production for the transport sector through fermentation (bio-alcohols) and transesterification (biodiesel) (Huber and Corma 2007; Cherubini 2010; Karatzos *et al.* 2014). The two processes have major roles to play as the need to reduce fossil related emissions has become critical. However, shortcoming from the use of traditional food crops must be addressed to achieve the 21st millennium development goals which include poverty alleviation and environmental sustainability (Amigun *et al.* 2011; Khan 2011; Pradhan and Mbohwa 2014). The threat posed by climate change has made it imperative to tackle environmental sustainability and one of the issues identified has been the high GHG emission from our transportation systems (Bessou *et al.* 2011). Expectation are that biofuels will play a key role in achieving energy security, poverty alleviation through agricultural activities to support the biofuel industry, reduced tailpipe emissions contributing significantly to the global goals (Wolde-Georgis and Glantz 2009; Bessou *et al.* 2011; Pradhan and Mbohwa 2014).

The number of vehicles dependent on petroleum fuels worldwide has been on the rise, this trend as well as a preference for private transport over public transport system has increased pressure on the exhaustible resource (Khan 2011). Emissions have risen drastically as a result with the 400 ppm threshold for CO_2 surpassed as of 2016 shown in Figure 3. The business as usual approach in the use of fossil fuel will surely put society on a path to catastrophic climate changes which is something the world has acknowledge through agreeing to pledges to work towards limiting the average temperature increase to below 2 °C [Paris conference agreement COP21] (Khan 2011; Yuan *et al.* 2015; Kahn 2016). The carbon budget is at a risk with scientist suggesting that about 1000 Gt carbon dioxide equivalent (CO_e) is left to burn and the current levels of 400 ppm CO_2 is said to have put us at about 1 °C increase in temperature of the 2 °C target set to avoid irreversible damaging impacts on the ecosystem (Khan 2011; Yuan *et al.* 2015; Kahn 2016) . Continuing along this path threatens the balance of ecosystem for the current and future generations thus emphasis and priority has been placed on moving to low carbon economies and society (Yuan *et al.* 2015; Kahn 2016).

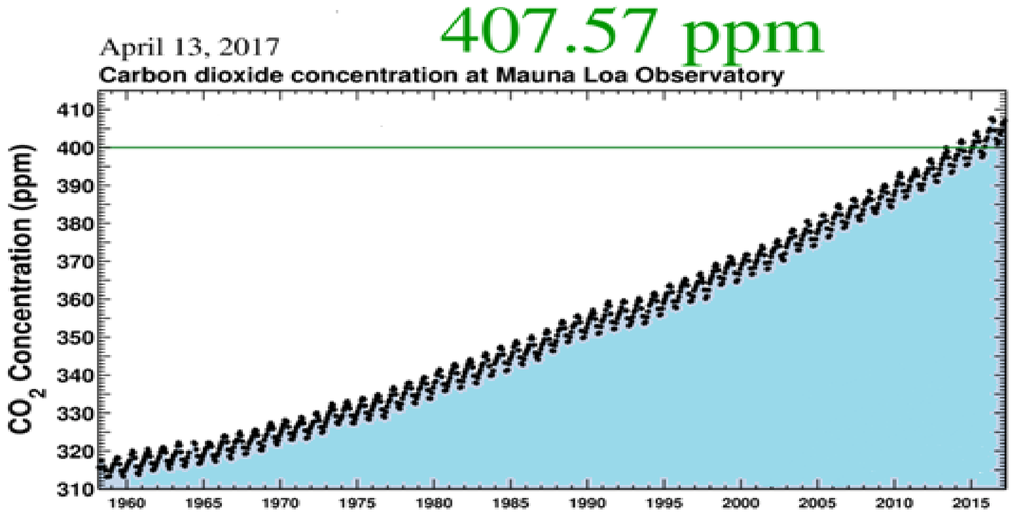

Figure 3, Cumulative CO_2 concentration, Source: National Oceanic and Atmospheric Administration (2017)

For the transportation sector, bioethanol and biodiesel are leading as the most used alternative fuels (Khan 2011; Karatzos *et al.* 2014). However, limitation based on these fuels based on physicochemical properties slightly different from petroleum derived fuels has made drop-in biofuel technology research and development key (Huber and Corma 2007; Karatzos *et al.* 2014). Biofuel attractiveness is due to the desirable properties of lower environment footprint, carbon neutrality, non-toxicity and biodegradable (Bessou *et al.* 2011; Karatzos *et al.* 2014). Biofuel drop-in alternatives will also release emission on combustion into the atmosphere, however the key point to note is their derivation from the natural carbon cycle allows for a balance to be restored during plant growth (photosynthesis process consumes CO_2) (Maher and Bressler 2007; Bessou *et al.* 2011; Islam *et al.* 2012; Karatzos *et al.* 2014). Burning fossil fuels on the other hand contributes to new entrants into the ecosystem released from millennia of captivity (Islam *et al.* 2012; Karatzos *et al.* 2014).

Suggestions have been put forth that plants prefer the light carbon C12 produced by plants over the heavy carbon C14 released upon combustion of fossilised fuels for the photosynthesis process (Islam *et al.* 2012; Karatzos *et al.* 2014). This may explain the build-up in CO_2 emission since the petroleum revolution which saw an increase in their use and production.

2.1.1 Alternative fuel

Alternative fuel vehicle running on electric power and biofuels have the potential to contribute to cutting emissions from the transportation sector which is currently contributing about a quarter of GHG emissions (Rye *et al.* 2010; Bhargava 2011; Karatzos *et al.* 2014). However, to-date the sale of electric vehicles is well below 1% of the global car sales and biofuel contribution has been pegged at less than 5% of the total liquid consumed (Karatzos *et al.* 2014; Hassan *et al.* 2015). Biofuels have been pegged back by feedstock production systems which so far have not been able to match the growing population needs in term of food production and have sufficient surplus for the industry (Rye *et al.* 2010; Karatzos *et al.* 2014; Xu *et al.* 2016). Finite nature of crude oil reserves and fluctuating oils prices were always important reasons to adopt alternative fuel options such as biofuels (Khan 2011; Karatzos *et al.* 2014). Lower oil prices and reduced subsidies for renewable energy have made the economic aspect of a lower carbon economy costly. A rapid drop in world oil prices for 2014-2015 from above $100/barrel to as low as $25/barrel had far reaching effects, with subsidies and incentives cut making it difficult to justify investment from an economic point of view. Transitions towards alternative fuels face a number of challenges relating to costs, refuelling infrastructure and consumer preferences (Khan 2011; Karatzos *et al.* 2014).

The primary alternative sources of energy systems that can replace fossil fuels are water, wind, solar energy and biomass (Khan 2011; Hassan *et al.* 2015). Biomass is gaining a great deal of attention in terms of supplying the world’s energy demand due to its abundant availability and environmental friendly nature (Rye *et al.* 2010; Bessou *et al.* 2011; Khan 2011). Environmentally friendly criteria are dependent on sustainable production of biofuel from cradle to grave analysis inclusive as some critics have highlighted that neglecting certain steps will lead to an oversight in the net emissions reduction (Bessou *et al.* 2011; Khan 2011; Islam *et al.* 2012).

A report by the IEA suggests that the transport sector will have to contribute about one fifth in GHG reduction if the 2 °C global average increase set at the Paris COP 21 is to be met (Clémençon 2016; International Energy Agency 2017). Alternative fuel for the transport sector should avoid the need for redesign of the internal combustion engine and distribution infrastructure for ease of consumer acceptability and economic benefit (Huber and Corma 2007). The drawbacks of the 1st generation biofuels have limited its market share penetration to less than 5% of the transportation fuel consumption worldwide, however projections point to a greater contribution as cellulosic ethanol production matures as well as other 2nd generation biofuel technologies (Huber and Corma 2007; Bessou *et al.* 2011; Karatzos *et al.* 2014). According to a recently released BP Statistical Review of World Energy report of 2016 there has been some progress in the production and use of 1st generation biofuels in the form of biodiesel and bioethanol as shown in Figure 4.

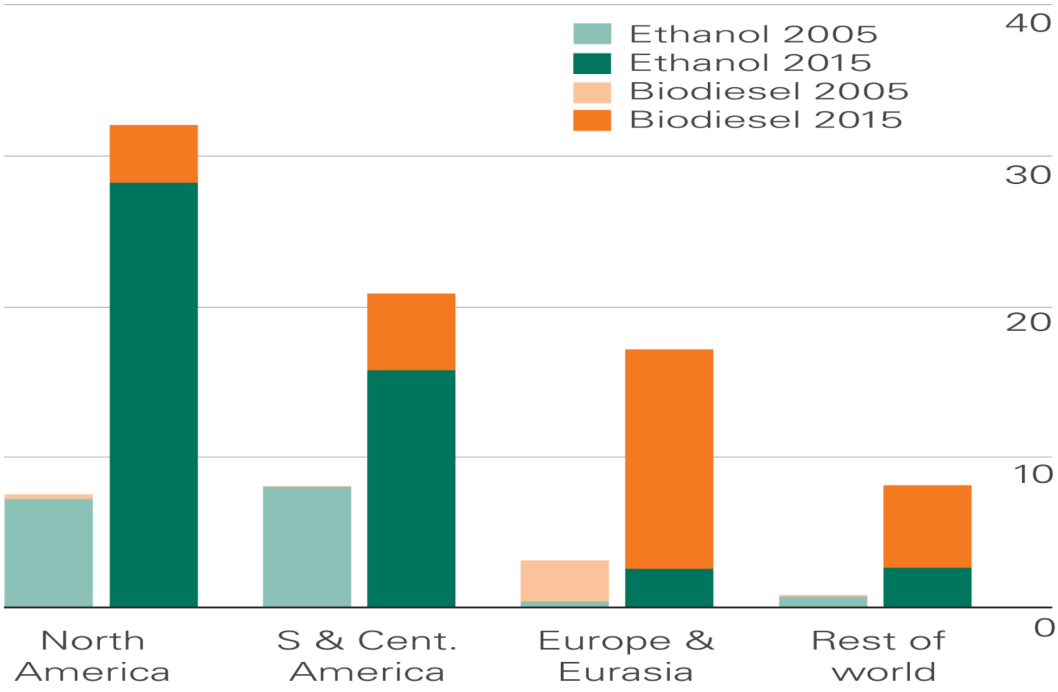

Figure 4, Biofuels consumption patterns, Source: British Petroleum Company (2014)

Despite the economic and social uplifting benefits that may be derived from a bio-based economy, the bioenergy industry has received intense criticism and negative reviews from certain sections of society citing land utilisation expansion which may have ramification with regards to biodiversity and sequestration of carbon (Huber and Corma 2007; Chen *et al.* 2010; Khan 2011; Islam *et al.* 2012). The use of bio-derived fuels is crucial in reducing the carbon footprint with the recent Paris climate deal chartering a direction towards low carbon economies and society if the planet is to be saved (Khan 2011; Islam *et al.* 2012).

Mandatory blending in different part of the globe has been put in place as a way of growing the biofuel sector (Khan 2011; Karatzos *et al.* 2014). However, there is need to develop the technology at the same pace to keep up with the increasing demand for liquid fuels (Islam *et al.* 2012; Karatzos *et al.* 2014). Potential benefits of transition towards a biofuel economy include economic, social and environmental (Islam *et al.* 2012; Karatzos *et al.* 2014). If operational cost of biofuel production is minimised, there is great potential to lower carbon footprint with increased usage (Khan 2011; Islam *et al.* 2012).

2.2 Motivation for a low carbon economy

The question has been how society can move to a low carbon economy with the continued increase in demand for energy and its direct bearing on economic growth (Khan 2011; Islam *et al.* 2012). Innovation and technology development will play a key role to address the challenges of moving to a low carbon economy (decarbonise the world economy) (Khan 2011; Islam *et al.* 2012). State of the art mature technologies are available to address emissions from the electricity sector in the form of hydro power, wind, nuclear and solar energy (Khan 2011; Islam *et al.* 2012; Karatzos *et al.* 2014). However the transport sector is heavily reliant on petroleum derived hydrocarbons thus the need to develop ways to produce alternative fuels that will contribute to GHG emission reduction (Rye *et al.* 2010; Karatzos *et al.* 2014).

There are claims and allegations that large petroleum corporates and oil producing countries have fought dirty to retain market competitiveness, continued exploration and production by dismissing legitimate claims of the influence of extensive use of fossil fuels (D’Angelo 2016). One such revelation has been brought to the society attention with a court case against ExxonMobil showing they had evidence on the influence of continued use of fossil fuels on climate change from as early as the 1970 (D’Angelo 2016). Increased awareness and pressure from the civil society will see an increased shift in policy and divestment from a heavily fossil oriented supply to a more sustainable energy mix (Karatzos *et al.* 2014; D’Angelo 2016).

Biomass derived energy has become a front-runner to augment and substitute petroleum derivatives with biodiesel and bioethanol currently in use as part of blends in the transportation sector (Huber and Corma 2007; Demirbas 2011). Their use has allowed for reduced emissions profile and there is still room for growth if affordable feedstock and efficiency synthesis procedure develops and matures (Karatzos *et al.* 2014). Research towards sustainable production of biofuels has increased with the focus being placed on two major areas of concern which are type of feedstock and catalyst preparation of highly active and selective systems (Hassan *et al.* 2015).

2.2.1 Environmental consideration (LCA)

Environmental and social acceptability of biofuel production is a key factor in developing biofuel support policies (Kurnia *et al.* 2016). Analysis of biofuel production routes has to critically analyse GHG emission saving and energy balance to determine the true sustainability of a process (Rathore *et al.* 2016). Life cycle assessment (LCA) which is an international recognised tool for determining the sustainability of biofuels has been applied on the different process route proposed for achieving low carbon in the transportation sector (Bessou *et al.* 2011; Khan 2011; Rathore *et al.* 2016). Feedstocks with high yields and non-food biomass have been proposed as best alternative to achieve higher net GHG savings (Khan 2011; Islam *et al.* 2012; Rathore *et al.* 2016). Significant attention has been placed on biofuels due to the potential they have in reducing GHG emissions while providing energy security.

Feedstock production systems are an important factor to note as the drive towards low carbon economies intensify with biofuel production a key piece to the puzzle (Islam *et al.* 2012; Pradhan and Mbohwa 2014). Contentious discussions and conflict surrounds the use of traditional food crops especially in developing countries (Amigun *et al.* 2011; Pradhan and Mbohwa 2014). The bulk of the current production routes for biofuels are primarily from cereals, grains, sugar crops and oil seeds (1^{st} generation biofuels) (Amigun *et al.* 2011; Pradhan and Mbohwa 2014). Increasing concerns have been expressed towards the sustainability profiles related to biofuel production through potential food vs. fuel competition, land-use change (through clearing forest for agricultural land) while those pro biofuel point to the potential economic and social development through poverty reduction and rural development (Amigun *et al.* 2011; Khan 2011; Islam *et al.* 2012; Pradhan and Mbohwa 2014).

Negative impacts of concern also include forest clearing (land-use change), loss of biodiversity, water scarcity and pollution from increased agricultural activities have also been raised (Amigun *et al.* 2011; Blanchard *et al.* 2011; Rathore *et al.* 2016). In Malaysia land-use change has become a major issue of concern with data showing that a lot of tropical forest has been cut down to increase land available for palm oil plantation which is a major feedstock for biofuel in the tropical countries due to its high yields (Chew and Bhatia 2008; Kurnia *et al.* 2016; Rathore *et al.* 2016). Fears are the plantations will not match the sequestration power for carbon as per previous rate when natural forests were in place thus resulting in a net positive GHG emission which will need to be paid off before potential environmental benefits are realised (Chew and Bhatia 2008; Kurnia *et al.* 2016; Rathore *et al.* 2016).

Sustainability covers several aspects, with important goals being to minimise the use of natural resources, production of toxic materials, emissions of hazardous pollutants and to improve energy efficiency (Rye *et al.* 2010; Rathore *et al.* 2016). Life cycle assessment is a tool that has been used to evaluate the major environmental impacts of a production process throughout the life cycle of the product (cradle to grave analysis) (Rye *et al.* 2010; Bessou *et al.* 2011; Kurnia *et al.* 2016; Rathore *et al.* 2016). The acceptance and reliability of an LCA depends on several factors among which the important one is the selection of the system boundary defining the production processes included and excluded from the analysis (Bessou *et al.* 2011; Kurnia *et al.* 2016). Land use change has been blamed for having the highest environmental impact through the expansion of land for agriculture purposes and the use of fertilisers to increase product yield (Blanchard *et al.* 2011; Kurnia *et al.* 2016).

Despite the fact that biomass can be produced continuously, the natural resources (land, water) limit the quantity that can be produced over a given period (National Academy of Sciences *et al.* 2009). Implications of utilising food crops as feedstock create a new dynamic on the market value of the produce from the agricultural activities with contributions from the food and fuel industry (Khan 2011; Islam *et al.* 2012). From the farmer's perspective higher prices means profitability of the farming activities but the rippling effect may lead to a strain on consumer purses (Wolde-Georgis and Glantz 2009; Blanchard *et al.* 2011; Khan 2011). Diverting traditional food crops for the biofuel sector has been said to be responsible for increased food, feed prices, however on the other hand the increase in crop prices will contribute to reviving rural communities (Karatzos *et al.* 2014; Pradhan and Mbohwa 2014). The limitations of traditional food crops with respect to attaining capacity yield and the need for external nutrients in form of fertilisers to boost yields puts sustainable production of biofuel from these resources in jeopardy (National Academy of Sciences *et al.* 2009; Karatzos *et al.* 2014).

This has seen the growth in research towards the utilisation of cellulose the major component of plant biomass to produce cellulosic alcohols (fermentation), biomass syngas (gasification) and pyrolytic oil (pyrolysis) (National Academy of Sciences *et al.* 2009; Demirbas 2011; Hassan *et al.* 2015). However, the product from the above mentioned processes are characterised by a higher oxygen content in comparison to petroleum derived fuels, thus there is need to upgrade increasing the H/C ratio to make it compatible with current combustion engine designs and specifications (National Academy of Sciences *et al.* 2009; Demirbas 2011; Hassan *et al.* 2015).

2.3 The South African case

The current energy mix in South Africa is heavily fossil oriented (Vanderschuren *et al.* 2008; Pradhan and Mbohwa 2014) . However history has shown that there have been periods of intense research and development to achieve energy security that have focused on bioenergy production (Vanderschuren *et al.* 2008). Isolation periods when crude oil imports to South Africa were banned led to the current energy mix heavily dependent on coal resources, however in line with the global community undertaking to reduce GHG emissions and tackle climate change renewable energy policies have been put in place (Vanderschuren *et al.* 2008; Pradhan and Mbohwa 2014). The Biofuel Industrial Strategy of 2007 was enacted to increase the penetration of the biofuels in the transportation sector which currently has been heavily dependent on oil imports and product of the Fischer-Tropsch synthesis utilising coal as feedstock (Vanderschuren *et al.* 2008; Pradhan and Mbohwa 2014). The heavy reliance on fossil oriented energy has seen South Africa being ranked no 14th in the world in term of CO_2 emissions and contributing more to the continent CO_2 emissions (ranked 1st on the continent) with current emission levels at over 440 Mt of CO_2 as shown in Figure 5 (Enerdata-Statistical-Yearbook 2017).

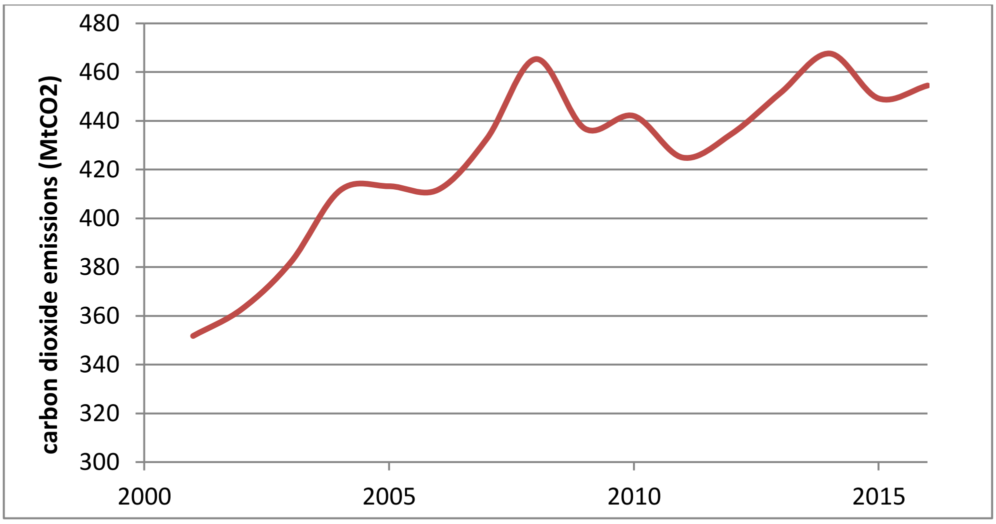

Figure 5, South Africa emission status, Source:Enerdata-Statistical-Yearbook (2017)

The Fischer Tropsch Synthesis has been harnessed to produce hydrocarbons from syn-gas (H_2+CO) derived from the thermal gasification of biomass or coal (Kang *et al.* 2011; Jahangiri *et al.* 2014). With the need for non-fossil derived fuels there is now growing interest in the use of FTS-processes to convert syn-gas derived from intractable biomass waste to liquid hydrocarbons for synthetic fuels and chemical feedstocks (Kang *et al.* 2008; Jahangiri *et al.* 2014). In South Africa the FTS process was established by South Africa Synthetic Oil Liquid (SASOL) in 1952 to take advantage of huge quantities of coal available in the country in order to reduce crude oil imports (Kang *et al.* 2008; Vanderschuren *et al.* 2008; Jahangiri *et al.* 2014). Synthetic fuel production in South Africa through SASOL contributes about 30% of the country's gasoline and diesel needs produced from syngas via FTS process (Kang *et al.* 2008; Vanderschuren *et al.* 2008; Jahangiri *et al.* 2014). The FTS process has allowed the transformation of various feedstocks into liquid products, including the gas-to-liquid (GTL), coal-to-liquid (CTL) and biomass-to-liquid (BTL) (Jahangiri *et al.* 2014). Synthetic fuel production has been an attractive process for countries lacking in crude oil reserve to meet the growing demand for liquid transportation fuels in an environment of limited oil supply (Vanderschuren *et al.* 2008; Jahangiri *et al.* 2014).

In order to contribute to the global effort to reduce emissions, South Africa has put in place policies such as the White Paper on Renewable Energy of 2003 with a view of diversifying the energy mix and the electricity generation sector has seen some progress with increased contributions from the solar and wind energy (Vanderschuren *et al.* 2008; Blanchard *et al.* 2011). The production and consumption patterns of crude oil shown in Figure 6 show a big net disparity between the petroleum needs of South Africa and what it can produce (International Energy Agency 2017). Huge import bill results from this scenario as shown in Figure 6 with a huge net import to cover, and this is true for many African countries where the transportation sector is heavily reliant on crude oil and corresponding emission profiles also increase (Vanderschuren *et al.* 2008). Most African nations have per capita emissions of below 1ton CO_2 while South Africa stands out with 7.2 ton due to its highly intensive industry and over reliance on coal (Clémençon 2016).

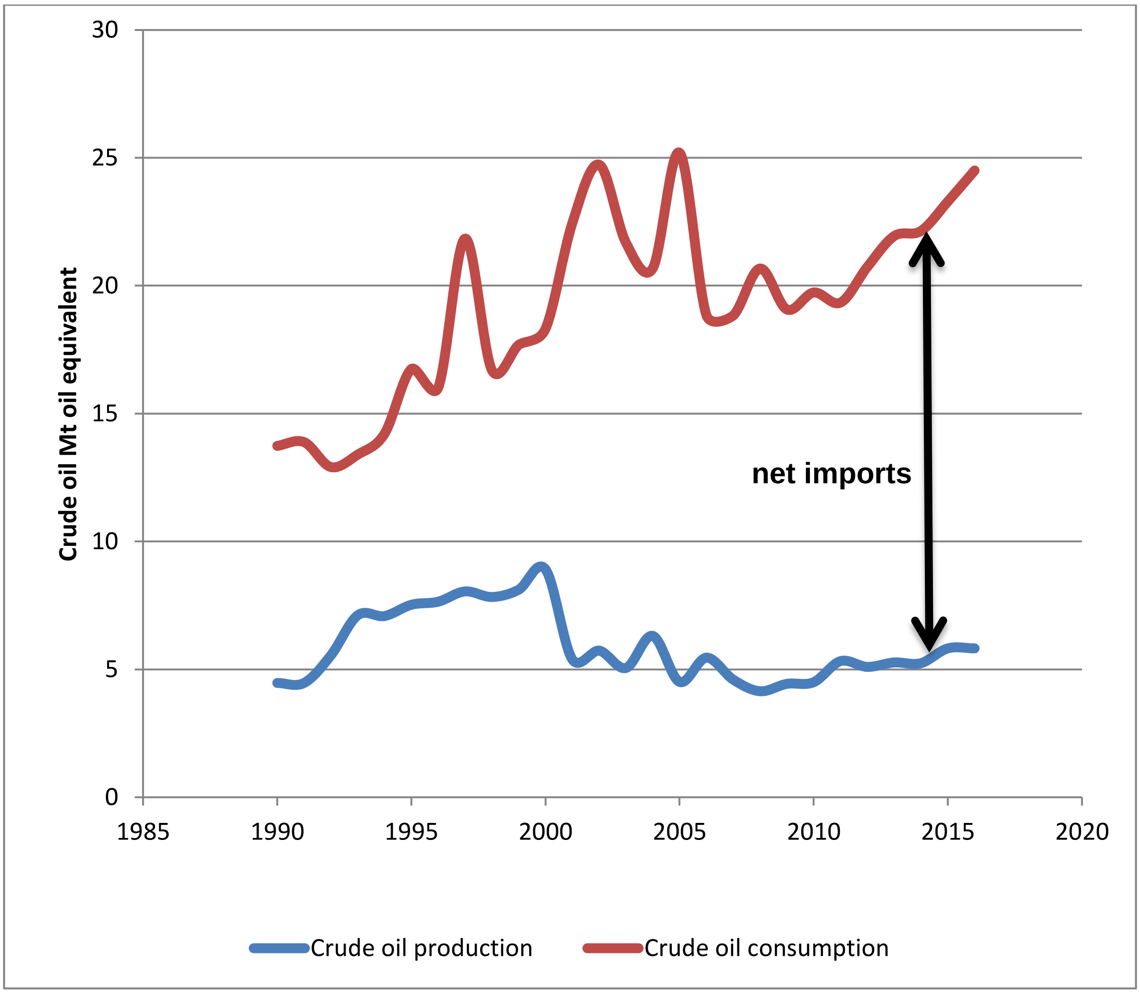

Figure 6, Consumption and production patterns for petroleum in South Africa, Source: Enerdata-Statistical-Yearbook (2017)

For the transportation sector, the Biofuels Industrial Strategy of 2007 was set to achieve a 2% penetration level of biofuels in the national liquid fuel supply (Vanderschuren *et al.* 2008; Amigun *et al.* 2011; Blanchard *et al.* 2011) with mandatory blending coming into effect as of October 2015. Certain crops were proposed for use in production of biofuels for mandatory blending which only came into effect in 2015 due to lags in implementation, the crops on the list are sugar cane, sorghum and sugar beet (for bioethanol) and sunflower, canola and soya beans (for biodiesel) (Vanderschuren *et al.* 2008; Pradhan and Mbohwa 2014). Maize and

Jatropha were excluded from the list for use in biofuel production for fear of interference with food security (Vanderschuren *et al.* 2008; Amigun *et al.* 2011; Pradhan and Mbohwa 2014).

The 2% level penetration target was set to allow for biofuel production with jeopardising food security and as per time of drafting of the policy this was supposed to take 1.4% of arable land in South Africa and in case of drought part of the produce would be redirected for food use (Vanderschuren *et al.* 2008; Amigun *et al.* 2011; Blanchard *et al.* 2011). The Biofuels Industrial Strategy of South Africa was developed to stimulate rural development and to reduce poverty by creating sustainable income-earning opportunities for marginalised communities (Amigun *et al.* 2011; Blanchard *et al.* 2011; Pradhan and Mbohwa 2014). Issues that arise from a South African perspective are the limitations placed on feedstock production as a result of limited arable which has been pegged at 14% and the fact that it is a water stressed country add to the biofuel dilemma for the country (Amigun *et al.* 2011; Blanchard *et al.* 2011; Pradhan and Mbohwa 2014).

2.4 Production of biofuel from biomass

Biofuels are often classified as first, second and third generation biofuels as shown in Figure 7. First generation biofuels utilise food crops as feedstock for biofuel production, while second generation biofuels utilise non-food biomass which is illustrated in Figure 7 (Naik *et al.* 2010; Bessou *et al.* 2011; Dutta *et al.* 2014). Third generation biofuels use algae and microbes as fuel source materials. To minimise the impacts of biofuel production on the environment, research has shifted towards the development of advanced biofuel technologies in the form of 2nd and 3rd generation biofuels (Naik *et al.* 2010; Dutta *et al.* 2014). Second (2nd) generation biofuels are characterised by higher GHG savings in comparison to the current commercialised biofuels which are bioethanol from fermentation and biodiesel from transesterification plus the processes are looking towards utilisation of non-food bio-feedstock (Naik *et al.* 2010; Bessou *et al.* 2011; Dutta *et al.* 2014). Critical analysis has to be taken on the energy input from fossil fuels to power the transformation process in order to determine the true value of the energy saving of the process as well as net CO_2 emission reduction (Dupont *et al.* 2009; Demirbas 2011; Dutta *et al.* 2014).

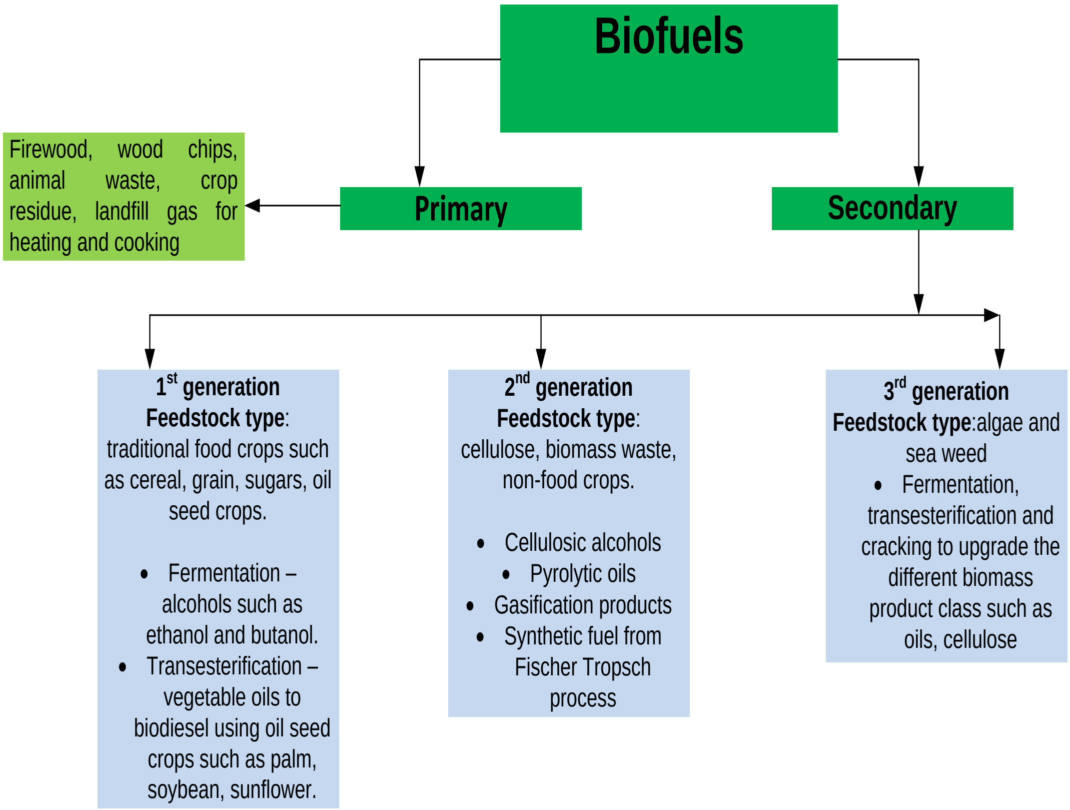

Figure 7, Classes of biomass derived fuels adapted from Dutta et al. (2014).

Numerous publications on biofuel production from plants oil are available in the current literature exploring the different thermochemical processing techniques available to improve the properties of plant oils to fuels (Yaakob *et al.* 2013; Emori *et al.* 2016; Kurnia *et al.* 2016; Shimada *et al.* 2016). Although virgin and food-grade oils have proven to be suitable feedstocks for biofuel production, the use of edible vegetable oils evokes the ‘food versus fuel’ debate on the use of widespread farmland areas for biofuel production in detriment of food supply (Mazubert *et al.* 2013; Talebian-Kiakalaieh *et al.* 2013; Teixeira *et al.* 2016). The use of non-edible crops, such as jatropha or castor oil, avoids the direct competition for food oils but does not resolve the problem of requiring large plantation land areas (Chen *et al.* 2010; Mazubert *et al.* 2013; Talebian-Kiakalaieh *et al.* 2013; Teixeira *et al.* 2016).

Waste cooking oil (WCO) as a potential renewable feedstock appears to be an economically and environmentally viable solution for biofuels production (Romero *et al.* 2016). It does presents a number of advantages: e.g. WCO is two to three times cheaper than virgin oils thus will reduce operational cost, the recycling of WCO reduces waste treatment costs and it can produce biofuels with the same quality as virgin oils (Mazubert *et al.* 2013; Talebian-Kiakalaieh *et al.* 2013). Despite its potential if not disposed of properly waste cooking oil could contribute to water and soil pollution, thus disturb the aquatic ecosystem as well as present human health concerns (Yaakob *et al.* 2013; Kurnia *et al.* 2016; Romero *et al.* 2016). Hence, rather than disposing it and harming the environment, it can be used as an effective and cost efficient feedstock for biofuel production as it is readily available and not create competition with other users or have an adverse impact on the food supply chain (Yaakob *et al.* 2013; Kurnia *et al.* 2016). Another challenge to be faced with the use of WCO utilisation is the collection systems from the various locations (restaurants, food factories and households) with most countries having no dedicated pipelines and systems in place (Kurnia *et al.* 2016; Romero *et al.* 2016).

2.4.1 Bioethanol

Ethanol the most widely used biofuel has mostly been produced from sugar and cereal crops (Galadima and Muraza 2015b). Production of ethanol an alcohol from biomass via fermentation of plant sugars is a well-established technology that has been employed for centuries (Chew and Bhatia 2008; Galadima and Muraza 2015b). However, due to sustainability issues with regards to the use of cereal (grain) crops and edible sugars which form part of the food chain, cellulosic fermentation development is on the increase (Chew and Bhatia 2008; Karatzos *et al.* 2014; Galadima and Muraza 2015b). Cellulose which form the bulk of plant material will allow for production of huge volumes of bioethanol when this technology fully matures (Galadima and Muraza 2015b). However, one of the major limitation of the fermentation products has been the high energy input required to make anhydrous bioethanol usable as transportation fuel (Karatzos *et al.* 2014; Galadima and Muraza 2015b).

Despite the acceptance of bioethanol as a fuel octane enhancer providing reasonable anti-knock properties; the lower energy density, lower vapour pressure (making cold starts difficult), miscibility with water limit their volume usage (about 10-15 vol % in blends) in conventional spark-ignition internal combustion engines (Narula *et al.* 2012; Galadima and Muraza 2015b). Ethanol use as an octane enhancer increased after the ban of leaded fuel (Narula *et al.* 2012; Karatzos *et al.* 2014; Galadima and Muraza 2015b). Adding bioethanol to gasoline increases the oxygen content of the fuel, improving the combustion of gasoline and reducing the exhaust emissions normally attributed to imperfect combustion in motor vehicles (Galadima and Muraza 2015b). Bioethanol has been used to augment the liquid fuel supply increasing the octane rating and lowering emission profiles (Chew and Bhatia 2008; Narula *et al.* 2012; Ramasamy and Wang 2014). Bioethanol has been used in various proportions as part of blends due to limitations of internal combustion engines designed to run on petroleum derived fuels (Galadima and Muraza 2015b).

The Brazilian experience has proven the economic sustainability of biofuel made possible through initial subsidy and incentives to grow the agricultural sector and the industry for conversion (Prado and Antoniosi Filho 2009; Galadima and Muraza 2015b). High ethanol production in Brazil and competitive pricing of the anhydrous ethanol for fuel use has allowed its extensive use in modified car engine known as flex fuel cars which may run on pure ethanol or blend with high volume percentage of alcohol (Prado and Antoniosi Filho 2009; Hassan *et al.* 2015). However, the majority of the cars on the roads worldwide rely on conventional fuels with flex fuel cars and electric cars contributing very little to the market (Bhargava 2011; Karatzos *et al.* 2014). Complete overhaul of the transportation systems to match ethanol and vegetable oil specifications will have a huge cost implication on the end user and car manufacturing industry (Karatzos *et al.* 2014).

Development of drop in alternatives to match the properties of conventional fuels has been explored in a manner similar to the methanol to gasoline (MTG) route utilising the bioethanol as the feedstock (Narula *et al.* 2012; Ramasamy and Wang 2014; Galadima and Muraza 2015b). Ethanol to hydrocarbons upgrade through the use of zeolites such as ZSM-5 has been researched by various researchers leading to the production of fuels with similar characteristics to conventional fuels (Narula *et al.* 2012; Ramasamy and Wang 2014; Galadima and Muraza 2015b). The performance of the zeolites has mimicked the MTG route resulting in fuels suited to substitute gasoline with high octane rated hydrocarbon composition as evidenced by the high aromatic content (Ramasamy and Wang 2014; Galadima and Muraza 2015b). Ethanol upgrade into the different fractions such as gasoline, kerosene and diesel via catalytic cracking results in a product with a higher gas mileage usable directly with no engine modification (Gayubo *et al.* 2010; Narula *et al.* 2012; Galadima and Muraza 2015b).

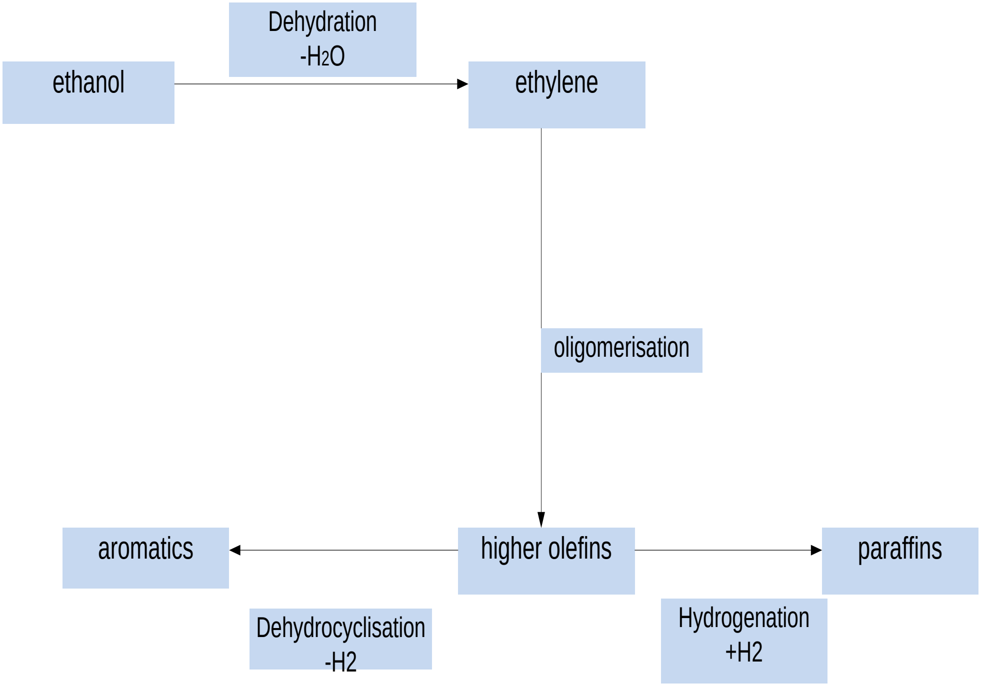

Figure 8, Ethanol catalytic upgrade over zeolites adapted from Ramasamy and Wang (2014)

The use of solid acid catalyst allows for processing of fermentation product with a high water content to potential drop-in fuel and base material for the production of synthetic materials i.e. chemicals and plastics (Gayubo *et al.* 2010; Karatzos *et al.* 2014; Galadima and Muraza 2015b). The proposed mechanism for the upgrade of fermentation alcohol through the use of acidic catalyst systems is suggested to follow the route shown in Figure 8. Zeolites acidity has proven to have a high selectivity towards the formation of aromatics hydrocarbons over paraffin's (Galadima and Muraza 2015b).

2.4.2 Plant (Vegetable) oils

Vegetable oils are produced from numerous oil seed crops and its use as transportation fuel is no new phenomena (Chhetri *et al.* 2008; Yaakob *et al.* 2013; Lam *et al.* 2016). The original design of Rudolf Diesel engine ran on peanut oil a vegetable oil and it was his belief vegetable oil would play a key role in society (Huber and Corma 2007; Chhetri *et al.* 2008). After a century dominated by fossil fuel use, sustainability and environmental aspects have forced society to revisit Rudolf's dream (Demirbas 2009; Karatzos *et al.* 2014; Hassan *et al.* 2015). His vision was to disassemble the monopolised energy and power industries through the use of farm produced oils as fuel and source of energy (Demirbas 2009; Lappi and Alén 2009; Demirbas 2011). The use of vegetable oil was abandoned due to the discovery of low cost petroleum reserve during the start of the 20th century (Huber and Corma 2007; Demirbas 2009; Hassan *et al.* 2015).

Modifications done on the engine design over the years due to the emergence of petroleum fuel as a major source of fuel for the transport sector has led to the application of vegetable oils becoming costly (Chen *et al.* 2010; Lam *et al.* 2016; Xu *et al.* 2016). Direct use of plant derived oils has been restricted due to high viscosity which leads to poor atomisation, high freezing point, incomplete combustion and carbon deposition leading to engine fouling (Demirbas 2009; Yaakob *et al.* 2013; Lam *et al.* 2016; Xu *et al.* 2016). Several techniques have been developed to transform biomass derived oils into acceptable fuels and these include; cracking (hydro, thermal and catalytic cracking), transesterification, micro emulsion as a way to improve the energy density and lower the viscosity (Demirbas 2011; Botas *et al.* 2012; Xu *et al.* 2016).

Numerous triglyceride sources are available for biofuel production with data showing that plant oil output rose to over 180 million tonnes in 2015 as shown in Figure 9 on the back of increasing palm oil output from countries such as Malaysia and Indonesia (Statista 2016; Xu *et al.* 2016). Current production rates of vegetable oil along with increased demand for the growing population means there is not enough to replace liquid fossil fuel (Yaakob *et al.* 2013; Lam *et al.* 2016). Non-edible oil and waste cooking oil offer potential to contribute without affecting food resource priority of the biomass material eliminating any possible controversy around threat to food security (Chew and Bhatia 2008; Demirbas 2009; Yaakob *et al.* 2013; Lam *et al.* 2016). Triglycerides are easier to convert into liquid transportation fuels than cellulosic biomass with higher energy content per unit volume as well as containing less oxygen (Lam *et al.* 2016; Romero *et al.* 2016; Xu *et al.* 2016; Wu *et al.* 2017).

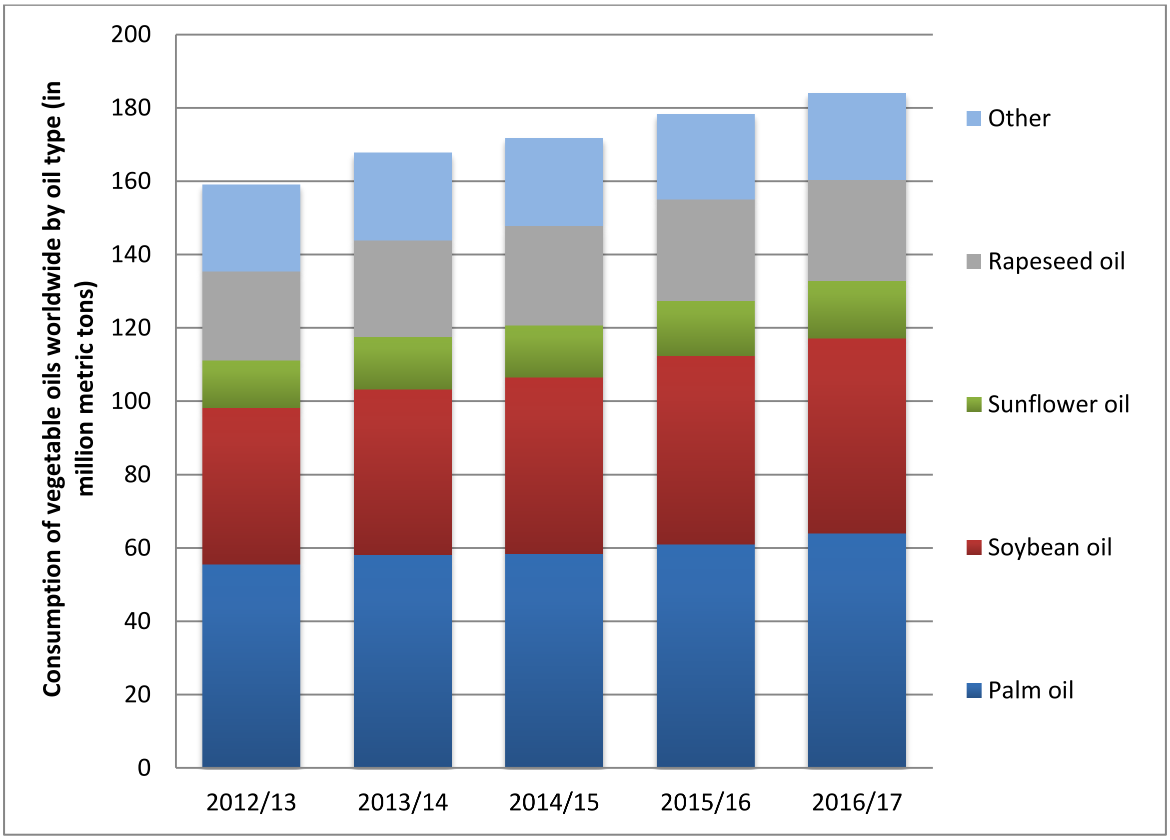

Figure 9, Consumption of vegetable oils worldwide, Source: Statista (2016)

Palm oil an edible vegetable oil is grown mostly in tropical countries in Southeast Asia and South America (Chew and Bhatia 2008; Kurnia *et al.* 2016). It has become the most consumed edible oil globally as shown in Figure 9, displacing soybean oil due to its high production efficiency but this has come at a cost, the growth has been coupled with increased forest loss in these tropical countries to increase plantation acreage (Chew and Bhatia 2008; Kurnia *et al.* 2016). Palm oil is considered the most efficient oilseed crop in the world due to its high productivity per hectare of about 4000 kg/ha (Chew and Bhatia 2008; Kurnia *et al.* 2016). Indonesia and Malaysia dominate the global production of palm oil, contributing around 85% of the palm oil production world-wide (Chew and Bhatia 2008; Kurnia *et al.* 2016). The industry has become a source of livelihood for the indigenous communities improving the quality of life and coupling the production of vegetable oil with biofuel production may have potential socio-economic benefits (Chew and Bhatia 2008; Kurnia *et al.* 2016). Despite the socio-economic benefits realised, negative reviews have surfaced based on land use change to increase production in line with increased demand (Chew and Bhatia 2008; Kurnia *et al.* 2016).

The future of sustainable biofuel production may lie in the utilisation of algae derived oil (Chen *et al.* 2010; Du 2013). However, the algae oil sector is still in its nascent stages with separation and recovery issue still to be resolved (Demirbas 2009, 2011; Du 2013). Microalgae have been recognised as promising sources of plant oils due their high productivity, high oil content and the ability to grow in a wide range of climates and lands (Chen *et al.* 2010; Du 2013; Lam *et al.* 2016). Algae as potential biofuel feedstock offer exceedingly high oil yields in contrast to terrestrial crops, minimal to no stress on water and land resources (Chen *et al.* 2010). Algae can be grown in contaminated waters, very marginalised land without the need for herbicides or pesticides as well as use of artificial fertiliser instead they utilise some of the nutrient rich waters for growth contributing to environmental protection (Demirbas 2009, 2011; Du 2013). The high growth cycle of algae could contribute significantly to the sequestration of CO_2 thus contributing more to reduction of GHG responsible for global warming (Chen *et al.* 2010). However this reality is still afar as the technology is still under research and development (Demirbas 2009; Chen *et al.* 2010; Demirbas 2011; Du 2013).

The use of non-edible oils for the production of biofuels will reduce the cost of processing significantly offering a chance of cost competitiveness in a market already dominated by mature petroleum processing (Yaakob *et al.* 2013; Lam *et al.* 2016; Romero *et al.* 2016). Inedible feedstock such as camelina, jatropha, waste cooking oil may prove to be important sources of feedstock for biofuels without competing for arable land and water resources and contribute positively to reducing carbon emissions (Chhetri *et al.* 2008; Demirbas 2009, 2011; Yaakob *et al.* 2013; Lam *et al.* 2016).

2.4.3 Transesterification

Transesterification is a process by which triglycerides (vegetable oil) react with an alcohol (methanol or ethanol) in the presence of catalyst to form fatty acid methyl/ethyl esters (biodiesel) and glycerol, (Chew and Bhatia 2008; Yaakob *et al.* 2013). The process has been deemed simple to operate utilising mild conditions (low temperature and pressure) and this has seen small scale production contribute to its continued growth in capacity (Lemoine 2013). For industrial purpose methanol has been adopted due to its reactivity and pricing (Chhetri *et al.* 2008). However, the use of renewable derived alcohols in the form of bioethanol has been identified in line with lowering the environmental footprint associated with biofuels production to increase the net GHG savings (Gayubo *et al.* 2010; Islam *et al.* 2012; Lemoine 2013).Traditionally the transesterification has been carried out with homogeneous base catalyst (Yaakob *et al.* 2013; Romero *et al.* 2016). It has been established that this class of catalyst is sensitive to free fatty acid and water content usually associated with non-edible oil such as rubber seed oil, jatropha and waste cooking oil (Chhetri *et al.* 2008; Yaakob *et al.* 2013). Another drawback from the use of homogeneous catalyst has been the increased cost of purification and separation as well as non-recovery of catalysts (Chhetri *et al.* 2008; Yaakob *et al.* 2013). This has seen increased research towards the use of heterogeneous catalyst systems such as zeolites, tungsten, and zirconia to overcome the constraints of the widely adopted homogeneous catalysts (Chhetri *et al.* 2008; Yaakob *et al.* 2013).

Most industrial applications on the use of triglycerides have focused on the production of diesel substitute through the transformation of vegetable oil to biodiesel by transesterification with either homogeneous or heterogeneous catalyst (Chhetri *et al.* 2008; Yaakob *et al.* 2013). Heterogeneous catalysis offers a number of advantages over homogenous catalysis and in particular, the ease of catalyst separation and the possibility to reuse and regenerate it (Chhetri *et al.* 2008; Talebian-Kiakalaieh *et al.* 2013). However, in industrial practice, heterogeneous catalysts are less widely used due to the high temperatures required, the problems related to catalyst leaching, and their sensitivity to FFA and water content (Mazubert *et al.* 2013; Talebian-Kiakalaieh *et al.* 2013; Yaakob *et al.* 2013). One of the main advantages of heterogeneous catalyst is that it allows WCO conversion with less strict requirements: catalysing the transesterification of WCO even if the FFA (<2 wt.%) and water content are greater than the limits required for conventional homogeneous base-catalysts (Lemoine 2013; Mazubert *et al.* 2013; Talebian-Kiakalaieh *et al.* 2013).

The products of transesterification are current contributing to the diesel substitution, one of the two major contributors along with bioethanol to the biofuel industry (Gayubo *et al.* 2010; Lemoine 2013). However, its wide adoption has been hampered by several undesirable characteristics which include lower energy density, relatively low thermal and oxidative stability making long term storage an issue (Chhetri *et al.* 2008; Lemoine 2013; Shimada *et al.* 2016). The undesirable characteristics have been linked to the degree of saturation as well as the oxygen content of transesterification product (biodiesel) and as will be discussed in the cracking section, deoxygenation of triglyceride may be lead to fuels with better properties (Shimada *et al.* 2016).

The industrialised processes have been utilising both edible and non-edible oil for the production of biodiesel, however as mentioned earlier the most adopted homogeneous catalyst have tolerance levels on FFA and water content (Chhetri *et al.* 2008). An issue may arise with the utilisation of waste cooking oil which is usually characterised with high water and FFA content due to hydrolysis of triglycerides during frying processes (Chhetri *et al.* 2008; Lemoine 2013). To address this more work is being done on the utilisation of heterogeneous, high FFA tolerant catalyst to produce biodiesel from cheaper non-edible feedstocks such as waste cooking oil (Lam *et al.* 2016).

2.5 Catalytic cracking

Cracking over different catalyst systems has proven to be the best route to get drop-in alternative fuels with several catalyst having been being explored such as zeolites ZSM-5, H-Y, MCM-41 (Huber and Corma 2007; Emori *et al.* 2016). Cracking allows for the production of drop-in alternative fuels and chemical precursor with a smooth transition in use as production and distribution networks from the existing petroleum refineries may be used lowering capital, human skills investment (Bhargava 2011; Botas *et al.* 2014; Karatzos *et al.* 2014). Drop-in fuels and chemical precursors will allow for a lower carbon society to be achieved without sacrificing engine operation performance while consumer acceptability will be easier (Karatzos *et al.* 2014; Hassan *et al.* 2015).

There is a wide variety of biomass types and process options available to produce fuels and chemical precursors; one key aspect has become the use of heterogeneous catalyst systems with tailored selectivity for products from renewable carbon feedstock (Huber and Corma 2007; Yigezu and Muthukumar 2014). Four main catalyst types have been use in catalytic upgrading of biomass feedstock which include transition metal catalysts, molecular sieve type catalysts, activated alumina, and sodium carbonate (Buzetzki *et al.* 2011; Yigezu and Muthukumar 2014; Romero *et al.* 2016; Teixeira *et al.* 2016). Studies done with non zeolitic material such as silica-alumina, metal oxide or carbonate on the cracking of biomass derived feedstock have yielded products with a high content of oxygenate hydrocarbons (Buzetzki *et al.* 2011).

The processing of biomass derived feedstocks through thermochemical techniques such as catalytic cracking and hydro-cracking has been identified as a faster way to transition to sustainable economies and society with less capital investment with infrastructure from petroleum refineries adopted (Huber and Corma 2007; Khan 2011; Yigezu and Muthukumar 2014; Wu *et al.* 2017). Catalytic upgrading has been used to convert high molecular weight plant based oils into lighter and more useful hydrocarbons, offering flexibility relative to the source of oil (Huber and Corma 2007; Khan 2011; Xu *et al.* 2016).

Cracking in the presence of hydrogen known as hydrocracking has also been studies and applied industrially over metal catalyst leading to a saturated product yield suitable as diesel substitute (Huber and Corma 2007; Emori *et al.* 2016; Xu *et al.* 2016). The presence of hydrogen allows for the deoxygenation of feedstock via hydrodeoxygenation resulting in no loss of carbon as compared to catalytic cracking where deoxygenation may occur via decarbonylation or decarboxylation leading to a product with one less carbon than the starting material as shown in Figure 10 (Emori *et al.* 2016; Shimada *et al.* 2016).

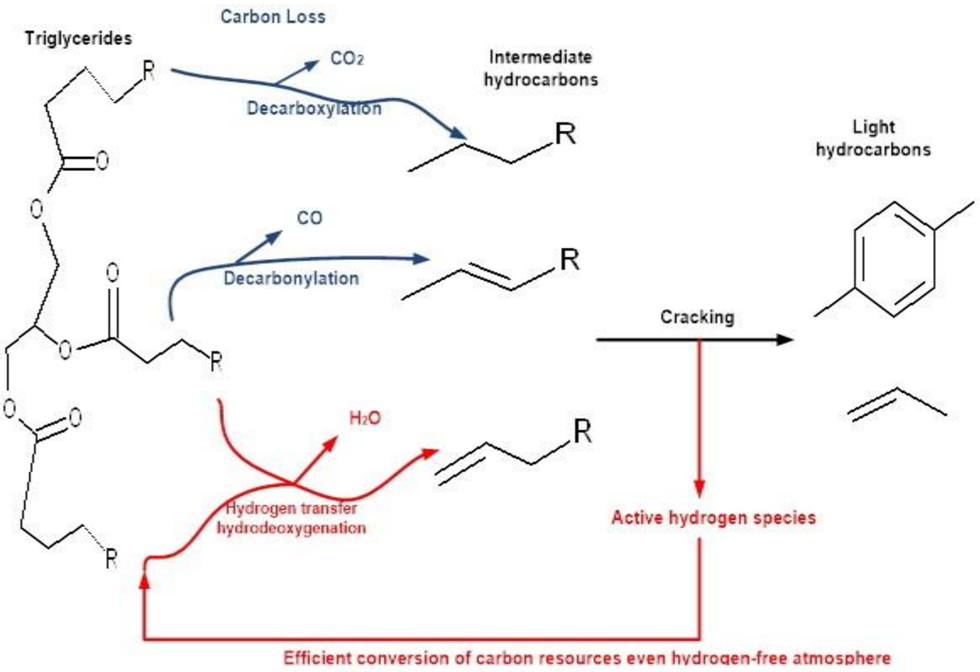

Figure 10, Triglycerides conversion proposed mechanism, Source: Shimada et al. (2016)

One of the main advantages of the hydrocracking is that the corresponding renewable fuel product is of high quality, oxygen free, hydrocarbon fuel with similar characteristics to conventional petroleum-based refinery fuel blend products (Huber and Corma 2007; Emori *et al.* 2016; Xu *et al.* 2016). To add onto this, current petroleum operations already have hydrocracking units in place thus bio-based feedstocks can be processed at refineries using existing equipment, thereby minimizing capital cost (Huber and Corma 2007; Teixeira *et al.* 2016; Xu *et al.* 2016). Transition metal catalysts and noble metal catalysts are common in the hydrocracking processes though a lot of work remains to be done to develop highly selective, environmentally friendly catalysts (Huber and Corma 2007; Emori *et al.* 2016; Xu *et al.* 2016). The drawback of hydrocracking lies in the high consumption of hydrogen which increases the cost of processing significantly (Emori *et al.* 2016; Shimada *et al.* 2016; Teixeira *et al.* 2016).

Cracking of vegetable oil consists of fragmentation of triglycerides of the oil, which take places above 500 K, with complete volatilization above 600 K and maximum decomposition rate at 685 K vegetable oil (Zandonai *et al.* 2016). In the study by Zandonai *et al.* (2016), the WHSV was varied from 2.5 h^{-1} to 4.5 h^{-1} with the minimal value leading to a maximum conversion. After the decomposition, the thermal effect of the reaction conditions influence deoxygenation and C-C scission of the free fatty acid chains also influenced to an extent by the acidity of the catalyst as well as the level of saturation of the fatty acid backbone (Emori *et al.* 2016; Zandonai *et al.* 2016). The influence of temperature on the cracking reaction has been found to promote an increase on conversion as well as aromaticity of product over acidic solid catalyst such as ZSM-5 (Emori *et al.* 2016; Zandonai *et al.* 2016). However, the yield of the organic liquid product decreases and yield of gaseous product increase (Emori *et al.* 2016; Zandonai *et al.* 2016).

An important characteristic of cracking catalyst is the acidity, and for the zeolite ZSM-5, the Si/Al ratio of the framework directly influences the acidity value and the characteristics of acid sites (Ahmad *et al.* 2016; Emori *et al.* 2016; Zandonai *et al.* 2016). Zeolite catalyst synthesis versatility allows for the Si/Al ratio of the framework to be altered, to influence the acidity of the catalyst, ultimately affecting product distribution (Ahmad *et al.* 2016; Emori *et al.* 2016). Acids sites interact with the hydrocarbons to accelerate the cracking process, therefore with lower Si/Al ratio (high acidity) the cracking activities are enhanced leading to higher gaseous product yield (Ahmad *et al.* 2016; Emori *et al.* 2016). In order to control the strength of the acid sites, bi-functional catalysts have been explored with the introduction of metals (Iliopoulou *et al.* 2012; Ahmad *et al.* 2016; Emori *et al.* 2016; Teixeira *et al.* 2016).

The presence of transition metals is suggested to affect the mode of oxygen rejection by producing more carbon oxides and less water, making that way more hydrogen available for incorporation into hydrocarbons (Iliopoulou *et al.* 2012). The metals introduced have a diluting influenced lower the strength of the strong Bronsted acid sites characteristic of zeolite material by introducing lower strength metal site (Lewis sites) (Iliopoulou *et al.* 2012; Emori *et al.* 2016; Teixeira *et al.* 2016). Transition metals deposited on zeolite support modify the acid and textural properties of the support (Ahmad *et al.* 2016; Emori *et al.* 2016; Teixeira *et al.* 2016). The combination of metal sites with acid sites of the zeolite gives rise to multi-functional properties to the catalyst (Iliopoulou *et al.* 2012; Ahmad *et al.* 2016). This gives rise to tailored selective product streams while shedding light on the complex mechanisms of catalytic reforming and cracking, which are still not well defined for biomass feedstock (Ahmad *et al.* 2016; Emori *et al.* 2016; Teixeira *et al.* 2016).

In the studies done by Botas *et al.* (2012); Botas *et al.* (2014), nickel (Ni) and molybdenum (Mo) modified hierarchical HZSM-5 was used to convert rapeseed oil producing olefins, aromatics and carbon nanotubes. Ni modified HZSM-5 catalysts showed enhanced dehydrogenation activity as denoted by increased hydrogen, olefins and carbon nanotubes (Botas *et al.* 2014). The dehydrogenation/hydrogenation influence of some of the metal dopants such as nickel enhances hydrogen transfer reaction promoting the production of high quality hydrocarbons without additional hydrogen consumption (Botas *et al.* 2012; Iliopoulou *et al.* 2012; Botas *et al.* 2014). Modification with iron created new strong acid sites with high susceptibility to coke formation and a reduction in the catalyst's pore-size lowering shape-selectivity properties (Iliopoulou *et al.* 2012; Galadima and Muraza 2015a).

Table 1, Energy density of various liquid fuels, Karatzos et al. (2014)

Fuel type	Energy density (MJ/kg)
Diesel	48
Petrol	45
Vegetable oil	42
Biodiesel	38
Butanol	36
Ethanol	30

It is important to deoxygenate biofuels as studies have shown that the oxygen content is directly related to the energy density which in turn determines the fuel tank size and travel range per unit quantity (Bhargava 2011; Karatzos *et al.* 2014). The data in the Table 1 shows that for petroleum processed fuels which have an almost zero content of oxygen, they had higher energy densities per unit quantity compared to biomass derived counterparts which can be substituted for fuel use (Bhargava 2011; Karatzos *et al.* 2014).

It is believed that triglycerides first undergo thermal and catalytic cracking on the external surface of the catalysts to produce heavy hydrocarbons and oxygenates (fatty acids) (Xu *et al.* 2016). Acidic zeolites have been known to promote cracking leading to olefinic intermediates which may undergo oligomerisation, isomerisation and aromatisation reactions depending on the properties of the acid sites available as well as porous structure (Emori *et al.* 2016; Xu *et al.* 2016). The widely acceptable mechanism of reaction discussed above is best summarised in the illustration in Figure 11. For the zeolite ZSM-5, this has been known to lead to a shape selective influenced product output with aromatics such as benzene, toluene, ethylbenzene and xylene expected to be present (Emori *et al.* 2016; Xu *et al.* 2016).

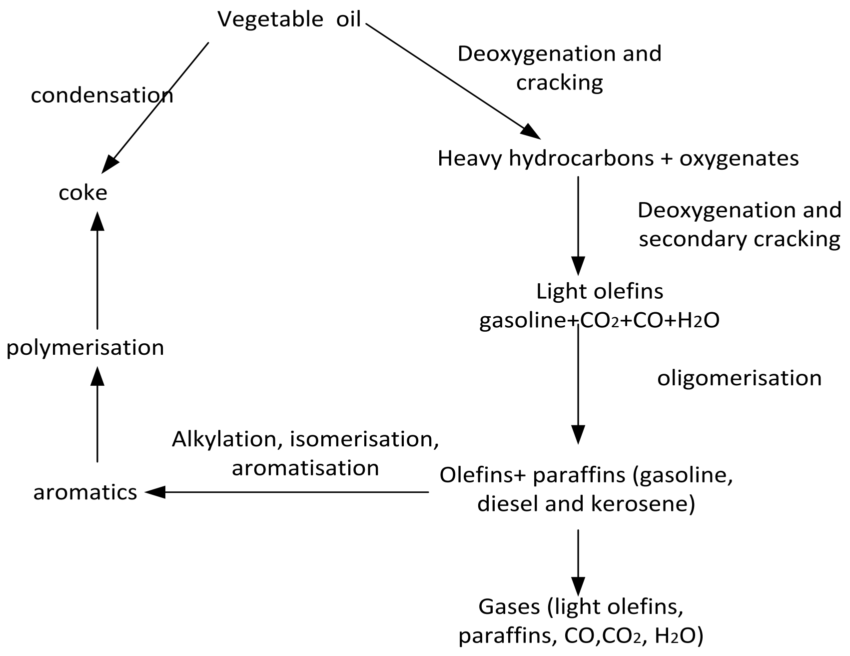

Figure 11, Schematic of proposed mechanism adapted from Idem et al. (1997)

2.6 The use of zeolite catalysts for biofuels production

The synthesis and integration of suitable zeolite based catalysts for biofuel production offering desired selectivity has become an area of interest for research and innovation (Davis and Li 2015; Ennaert *et al.* 2016). The molecular sieve catalyst have become the most widely used catalysts for catalytic upgrading of biomass feedstock finding applications in trigylcerides, bio-oil and ethanol upgrading processes to fuel range hydrocarbons (Buzetzki *et al.* 2011; Davis and Li 2015; Ennaert *et al.* 2016; Xu *et al.* 2016). A variety of molecular sieve catalysts with different pore sizes and pore structures have been studied in the conversion of biomass derived feedstock to fuels (Buzetzki *et al.* 2011; Davis and Li 2015; Xu *et al.* 2016). Although HZSM-5 catalysts are promising, they have exhibited high gas formation, which decreases the formation of the desired liquid fraction (Davis and Li 2015; Ennaert *et al.* 2016; Xu *et al.* 2016). Different types of catalysts have been studied in attempts to minimize the gas fraction and maximize the liquid fraction (Ennaert *et al.* 2016). It has been observed that mesoporous materials such as MCM-41 provide favourable selectivity toward particular liquid hydrocarbons, such as gasoline, kerosene, or diesel (Davis and Li 2015; Ennaert *et al.* 2016; Xu *et al.* 2016). Mesoporous catalyst have also shown a high selectivity towards diesel range hydrocarbons while zeolite ZSM-5 has been effective at converting biomass feedstock to liquid gasoline range hydrocarbons (Davis and Li 2015; Ennaert *et al.* 2016; Xu *et al.* 2016).

The morphology of the crystals is important because it can influence the activity and selectivity of the zeolites as catalysts (Davis and Li 2015; Ennaert *et al.* 2016). Accessibility to the active sites, shortening of the diffusion path length in the micropore can increase the activity and/or the selectivity for some products of the catalysts and increase the catalytic lifetime (Weitkamp and Puppe 2013; Davis and Li 2015). Catalyst life of zeolites is largely dependent on their pore structure. ZSM-5 shape selectivity prevents the formation of the transition state needed for the transfer of hydrogen hindering bi-molecular interactions which lead to coke formation in the micro-porosity of the catalyst (Rahimi and Karimzadeh 2011; Davis and Li 2015; Ennaert *et al.* 2016).

Several techniques have been developed to characterise the synthetic zeolite material used in the catalytic upgrading of biomass derived feedstocks. Important characteristics for catalytic material include surface area and pore topology, the strength of acidity which may influence the activity and selectivity of the catalytic upgrading process of ZSM-5 catalyst. The X-ray diffraction (XRD) analysis, a powerful non-destructive technique has been used to identify the developed synthetic crystalline material based on the periodic atomic arrangements differentiating amongst the family of zeolite catalysts (Davis and Li 2015). Database of the different patterns have been created to assist in the identification of the crystalline material (Treacy and Higgins 2007). The prepared catalyst synthesised in this study produced fingerprint patterns matching the MFI form of ZSM-5 zeolite as well as monoclinic or orthorhombic crystal lattice structure confirmed from Miller indices (Treacy and Higgins 2007; Yaripour *et al.* 2015).

The shape selective properties of zeolite material based on the distinct porous structure offers challenges with regards to the locations of active sites and the typical model of ZSM-5 is shown in Figure 12 (Ennaert *et al.* 2016). In order to harness the shape selectiveness of the catalyst in the production of valuable petrochemical feedstocks such as benzene derivatives, the location and strength of active sites is of importance (Ennaert *et al.* 2016). It has been realised that having the greater majority of active site within the microporous structure of ZSM-5 zeolite leads to enhanced shape selectivity, leading to a product with high aromatic compounds (Davis and Li 2015; Ennaert *et al.* 2016). In order to maximise shape selectivity, the intra-crystalline voids of the catalysts need to be maximised with the external surface contribution minimised (through making the external surface area small) (Weitkamp and Puppe 2013; Davis and Li 2015). Crystalline size has an influence on the distribution of active site on the interior and exterior surface area of the catalyst system thus influencing shape selectivity (Davis and Li 2015; Ennaert *et al.* 2016).

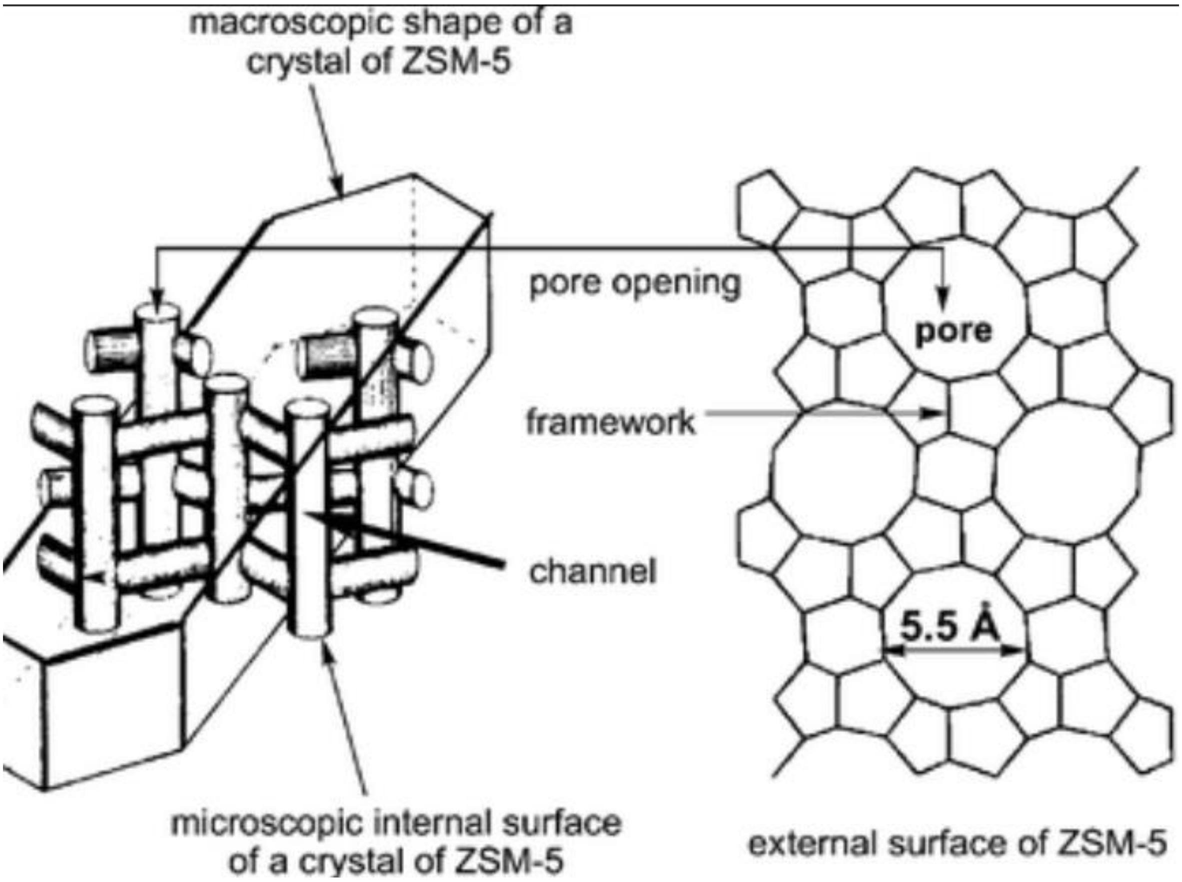

Figure 12, ZSM-5 model schematic, Source: Bhatia (1989)

Although ethanol has been used in blends with gasoline for combustion in internal combustion engines, it has been pointed out that this blend fuel may be responsible pollution through the release acetaldehyde and evaporative emissions (Gayubo *et al.* 2010; Galadima and Muraza 2015b; Wang *et al.* 2015). This has seen increased research towards ethanol to gasoline (ETG) conversion carried out (Ramasamy and Wang 2014; Wang *et al.* 2015). Success of this process has been modelled on the methanol to gasoline (MTG) process pioneered by Exxon Mobil in Canada which saw the major works being done with zeolite ZSM-5 to produce high octane rating hydrocarbons (Galadima and Muraza 2015b). Partly due to some similarity in the catalytic upgrading intermediate mechanisms of ethanol, pyrolysis and triglycerides, co-processing potential has been identified with the study by Wang *et al.* (2015) an example. The study looked at the conversion of ethanol and model bio-oil compounds over metal modified HZSM-5, with product selectivity being highly aromatic and olefinic in nature (Wang *et al.* 2015). The presence of ethanol in the co-cracking process was said to aid with the provision of surplus hydrogen from the cracking of ethanol, acting as a donor for the hydrogen transfer reactions characteristics of acidic zeolite catalysts leading to a highly aromatic yield (Wang *et al.* 2015).

2.7 Chapter summary

The upgrading of renewable based carbon derivatives such as bio-oils, triglycerides and ethanol presents an alternative way to produce high-quality hydrocarbons (transportation fuels and petrochemicals) with limited overall environmental carbon footprints (Gayubo *et al.* 2010; Valle *et al.* 2010; Ennaert *et al.* 2016). Considerable advantages of catalytic upgrade to drop-in alternatives include ease of integration into storage and transportation infrastructure as well as the potential to supply a number of valuable petrochemical feedstock (Taufiqurrahmi and Bhatia 2011). Drop-in biofuels eliminate the short shelf-life defect of both ethanol and biodiesel (Emori *et al.* 2016). Through catalytic conversion over acidic zeolites, deoxygenation of biomass derived feedstock may occur to produce liquid fuels rich in aromatics as highlighted in the research studies done by Taufiqurrahmi and Bhatia (2011); Ennaert *et al.* (2016); Emori *et al.* (2016).

Metal/zeolite bifunctional catalysts have been investigated in the upgrading of biomass derived feedstock to harness the influence of active centres contributed by the metal sites as well as acidic sites associated with zeolite material (Gayubo *et al.* 2010; Ennaert *et al.* 2016). Considering the fact that Bronsted acid sites for zeolites are mostly located inside the micropores, the importance of micropore volume on activity and selectivity should not be ignored as was mentioned in the study by Baradaran *et al.* (2015). Acidity strength increases the occurrence of hydride transfer reactions alongside cracking.

In a study by Chen *et al.* (2010) over different zeolite catalysts, the MFI structured zeolite show a greater selectivity towards aromatic compounds from the conversion of canola oil with values as high as 76.9 % recorded. Thermal cracking experiments carried out by Lima *et al.* (2004); Prado and Antoniosi Filho (2009); Chen *et al.* (2010) show that higher organic liquid product result from the treatment of triglycerides in the absence of catalysts. However, characterisation analysis done on the products show that the products are highly oxygenated limiting their application as possible alternatives to conventional products (Lima *et al.* 2004; Prado and Antoniosi Filho 2009; Chen *et al.* 2010).

The current study focuses on the utilisation of triglycerides (waste cooking oil) and ethanol (fermentation product) mixture over the molecular sieve zeolite HZSM-5, and the influence of creating bi-functional catalyst systems through doping with metals iron and nickel. Co-cracking of ethanol with vegetable oil will allow for production of drop-in alternative (Zhang *et al.* 2012; Wang *et al.* 2015). Zeolites such as ZSM-5 have proven to be hydrothermally stable allowing for use of feed with levels of water that would be intolerable in engine fuels or in a process such as transesterification (Gayubo *et al.* 2010; Zhang *et al.* 2012). Ethanol has been found to have better solvent properties than methanol, forming a single phase with vegetable oil (Ramasamy and Wang 2014; Galadima and Muraza 2015b; Wang *et al.* 2015). The lower polarity of ethanol in contrast to methanol allows for the non-polar vegetable oil to dissolve better forming a homogeneous mixture (Galadima and Muraza 2015b).

Chapter 3

3 Research Methodology

3.1 Methodology

Experimental work done during the course of this study was broken down into two phases which involved;

-1) Preparation and characterisation of the aluminosilicate catalysts, and 2) Conversion of ethanol-waste cooking oil mixtures over the synthesised catalyst as well as product analysis,

3.1.1 Equipments used for the study.

The following equipment was used during the course of the study in the synthesis, characterisation and test activity of synthesised catalyst;-

- Overhead stirrer for gel preparation
- Oven for crystallisation and drying
- Muffle furnace for calcination
- Tube furnace
- HPLC pump for the feed to the reactor
- The reactor was designed from ½ inch stainless steel tubing acquired from Swagelok along with the connector and reducer components to complete the circuit from the pump and to the condenser section.

The following characterisation equipment was used during the course of the study,

- Scanning electron microscope (FEI Nova NanoSEM 230 model)
- EDS detector (Oxford X-Max model)
- X-ray diffractometer (BRUKER AXS D8 Advance model)
- Brunauer–Emmett–Teller (Micromeritics TriStar II 3020)
- Gas chromatography-mass spectrometry (GC-MS QP 2010 Ultra by Shimadzu)

Figure 13 shows the schematic of the experimental work carried out in this study.

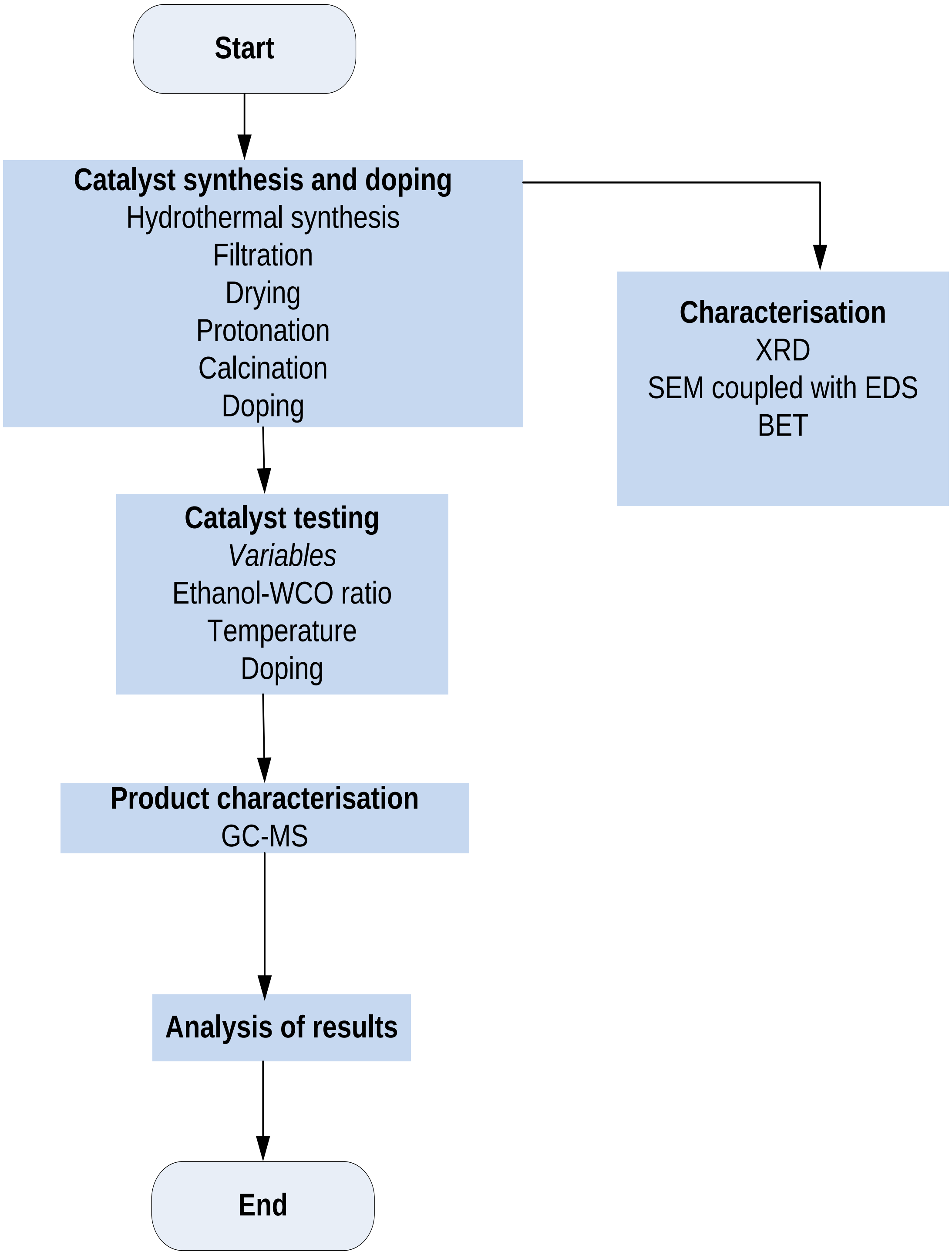

Figure 13, Schematic for the experimental study

3.1.2 Catalyst preparation

Starting material for the synthesis was obtained from Sigma Aldrich and the materials included sodium silicate (Na_2O~10.6%, SiO_2~26.5%), aluminium nitrate, tetra-propyl-ammonium bromide (TPABr), nickel (II) nitrate hexahydrate, iron (III) nitrate nano-hydrate, nitric acid and ammonium nitrate. The steps taken during the synthesis were as follows; - gel preparation, aging, hydrothermal treatment, product recovery through washing and vacuum filtration, drying, calcination, protonation and promotion.

The aluminosilicate catalyst was prepared by hydrothermal crystallisation under autogenous pressure with an aging period of 24 hours and a set crystallisation time of 48 hours at set temperature of 170 °C (Baradaran *et al.* 2015). The gel was prepared from the alumina, silica and template sources added to pre-determined volume of water mixed in plastic beakers until a smooth gel was achieved under stirring with the following molar composition **Al_2O_3: 50 SiO_2: 19 Na_2O: 4 TPA^+: 2000 H_2O**. After achieving a homogeneous gel mixture in the pH range of 10.6 -11, adjusted through the use of nitric acid, the contents were transferred to Teflon lined stainless steel autoclaves to age (Baradaran *et al.* 2015). After the crystallisation period the contents of the Teflon cup were recovered and washed several times with distilled water to a pH of between 7 - 8, under vacuum filtration on a Buchner funnel and oven dried at 110°C for a period of 12 hours (Baradaran *et al.* 2015). The protonation was carried out by ion exchange with 1 mol/L ammonium nitrate, 10 % solid content, under stirring for 2 hours at 80 °C (Baradaran *et al.* 2015). After filtration to recover the solid material, it was rinsed with distilled water and dried at 110 °C with the last step calcination at 500 °C for 5 hours in static air (Baradaran *et al.* 2015). The metals (Fe and Ni) was introduced to the prepared catalysts by incipient wetness impregnation with the volume of precursors nitrate determined by the method used in the study by Teixeira *et al.* (2016). After impregnation, the catalysts were dried at 110 °C for 12 hours and calcined in a muffle furnace at 550 °C under static air for 4 hours (Baradaran *et al.* 2015). In order to avoid accidental seeding from residue in the Teflon cups, cleaning was done through the use of warm aqueous sodium hydroxide of 1 molar (1M) concentration for 4 hours before synthesising a new batch.

The illustration Figure 14 shows the major steps taken in the preparation of the catalyst system, image A of the illustration showing homogenous gel preparation making use of an overhead stirrer to achieve homogeneity. The nitric acid pH adjusted and aged gel was transferred to Teflon lined autoclaves before crystallisation under static conditions in a laboratory oven as shown in image B of the illustration. After the crystallisation period, the solid powder (image C) is recovered from the crystallisation gel. The recovered solid powder is calcined to remove the organic template in a muffle furnace under static air shown in image D of the illustration below.

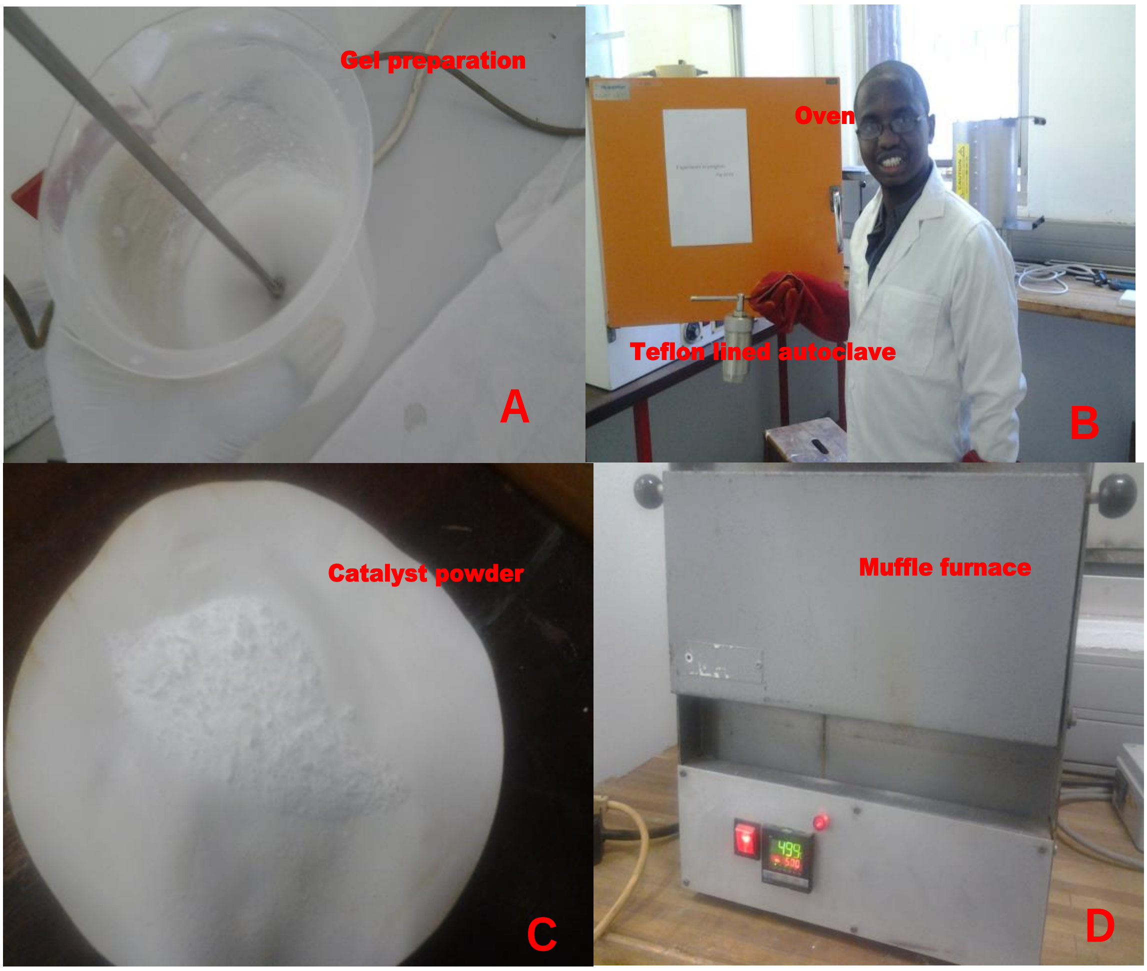

Figure 14, Synthesis illustrated in pics

3.2 Catalyst characterisation

The zeolite ZSM-5 synthesised with a SiO_2/Al_2O_3 target ratio of 50 was tested for activity in the conversion of ethanol-waste cooking oil mixture before and after doping with promoter metals nickel (Ni) and iron (Fe). The hydrothermally synthesised crystalline material produced was subjected to a number of characterisation techniques to determine its identity and these included; -

- X-ray diffraction (XRD)

To determine phase purity and identify the material based on its characteristic diffraction pattern a D8 Advance diffractometer was employed. XRD measurements were taken in a BRUKER AXS diffractometer using Cu-Kα (1.5406 Å) radiation with step size and counting time of 0.034° and 96s, respectively in the range 3 -89.9° of 2θ values

- Scanning Electron microscopy

The morphological structure of the crystal was studied under a FEI Nova NanoSEM 230 field emission gun using high resolution immersion lens. The samples were prepared by sprinkling a small amount of ZSM-5 catalyst onto an aluminium SEM stub and covered in carbon glue. The excess samples was blown off with compressed air and the samples were carbon coated before loading into the SEM to develop micrographs at set magnification as shown in chapter 4.

- Energy Dispersive X-ray spectroscopy

Approximate elemental composition was determined using the Oxford X-Max EDS detector by taking snap shots of the sample material for analysis.

- Brunauer–Emmett–Teller (BET)

The BET surface area, micropore specific area and volume (t-plot model) was determined from nitrogen adsorption/desorption isotherms measured at −196 °C using a TriStar II 3020 Micromeritics apparatus for the prepared catalyst material.

3.3 Catalyst testing

The developed solid acid catalyst was tested over a fixed bed reactor system with the ethanol-WCO mixtures as feedstock in increments of 25% WCO in the mixture as well as runs done on 100%WCO. The following identification codes was used throughout the text to denote the solid acid catalyst developed and these are HZSM-5 (for parent catalyst system), NiHZSM-5 (for nickel doped catalyst) and lastly FeHZSM-5 (for iron doped system). The test activity yielded gaseous and liquid product (organic and water) however the focus of analysis and characterisation through GC-MS was placed on the organic liquid product.

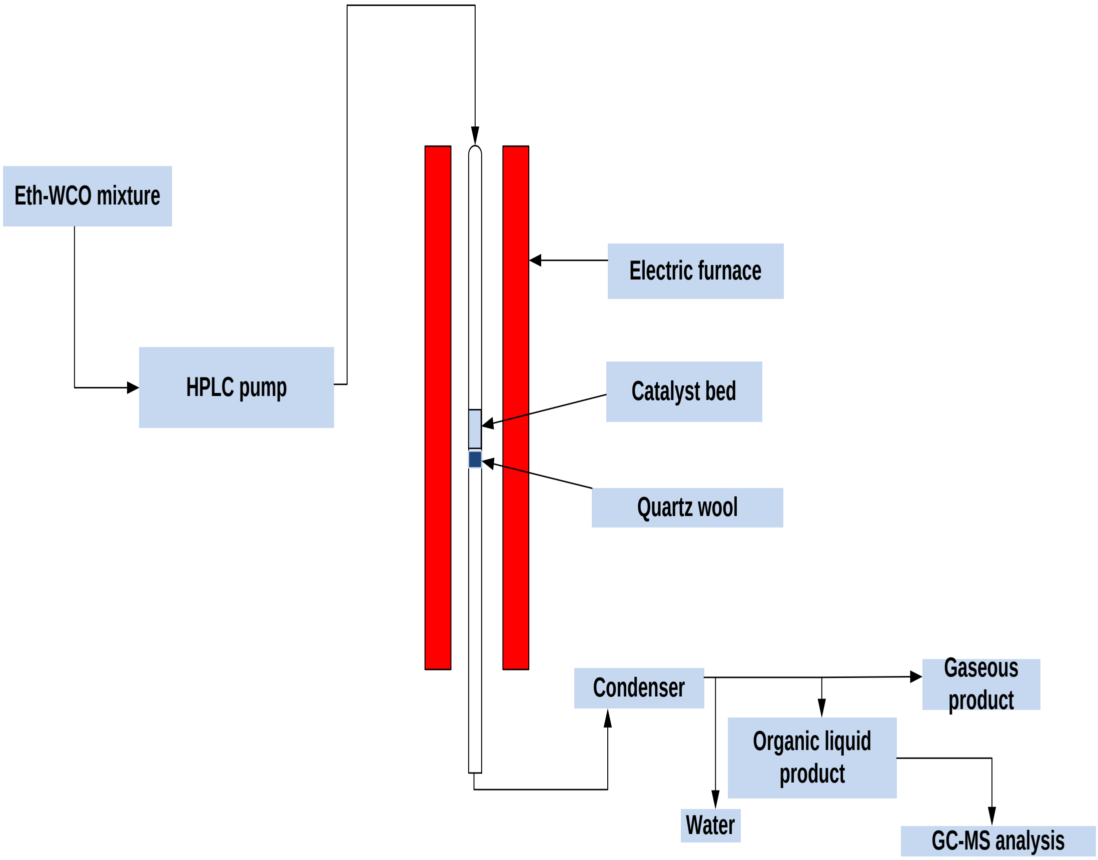

Figure 15, Schematic diagram of experimental installation for catalytic upgrade of mixture

The system mainly consists of the following parts; magnetic stirrer to keep feed mixture homogeneous, HPLC pump for feed injection (operability 0.01–5 cm^3 min^{-1}) , tube furnace, reactor with catalyst for conversion, condenser and product recovery section. The mixture was fed at a weight hourly space velocity of 2.5 h^{-1} for a period of 4 hours using an HPLC pump. To allow for uniform heating within the catalyst bed before feed input, preheating of the reactor was done at 500 °C for an hour. The reaction temperature was controlled by a thermocouple placed right at the centre on the outside of the stainless steel tube reactor where the catalyst bed was located. Due to the high thermal conductivity of stainless steel, the temperature different was assumed to be negligible expected to be not greater than 5 °C. To counter the effect of pressure drop or increase within the system, a low catalyst powder catalyst loading of 0.5 g was used in the experiment as well as the use of an HPLC pump with a greater capacity to pump against pressure systems. To avoid cold spots during the duration of the experiment, quartz wool was used to insulate the top and bottom void spaces between the furnace and reactor tubing. The gaseous product flowrate was measured by a gas flow bubble meter after every 15 mins and the averages values taken for recording.

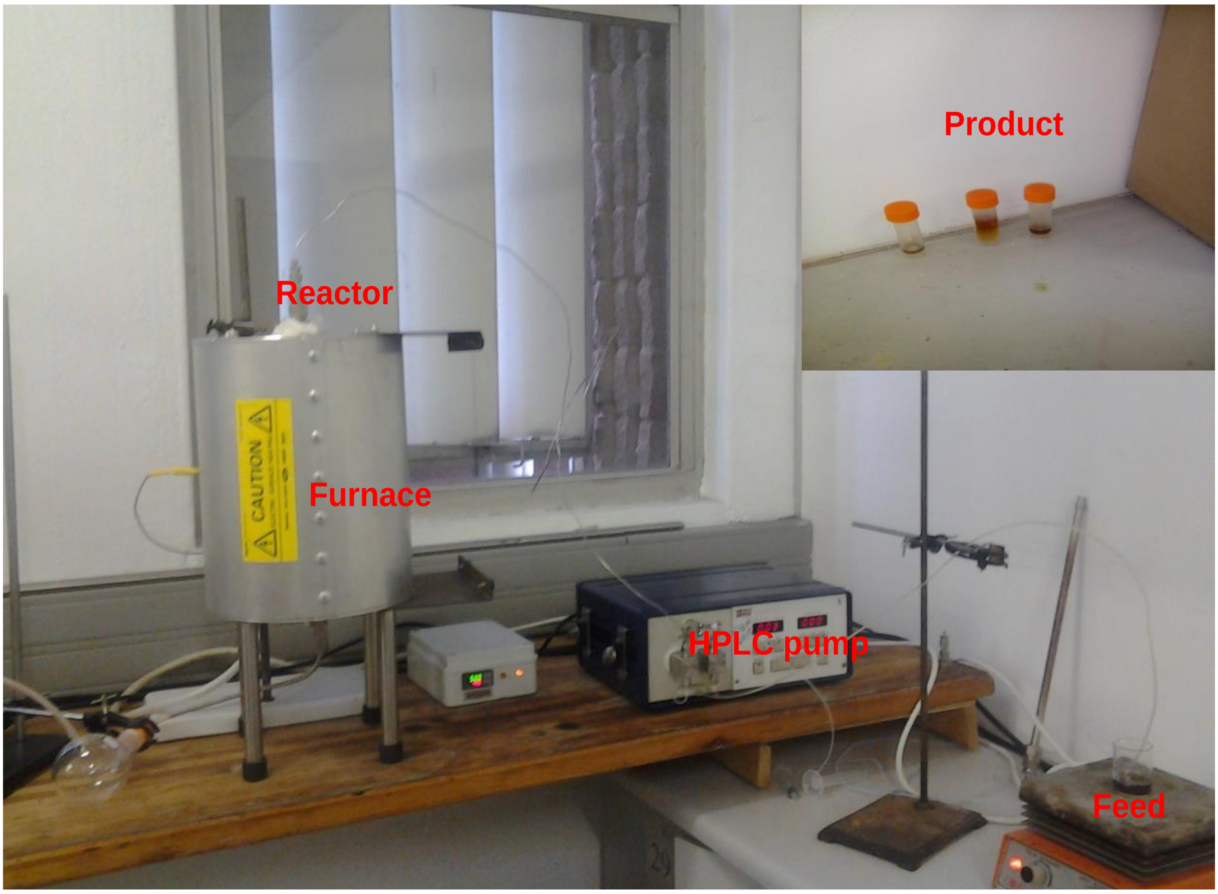

Figure 16, Experimental setup for the study

3.3.1 Product characterisation with GC-MS

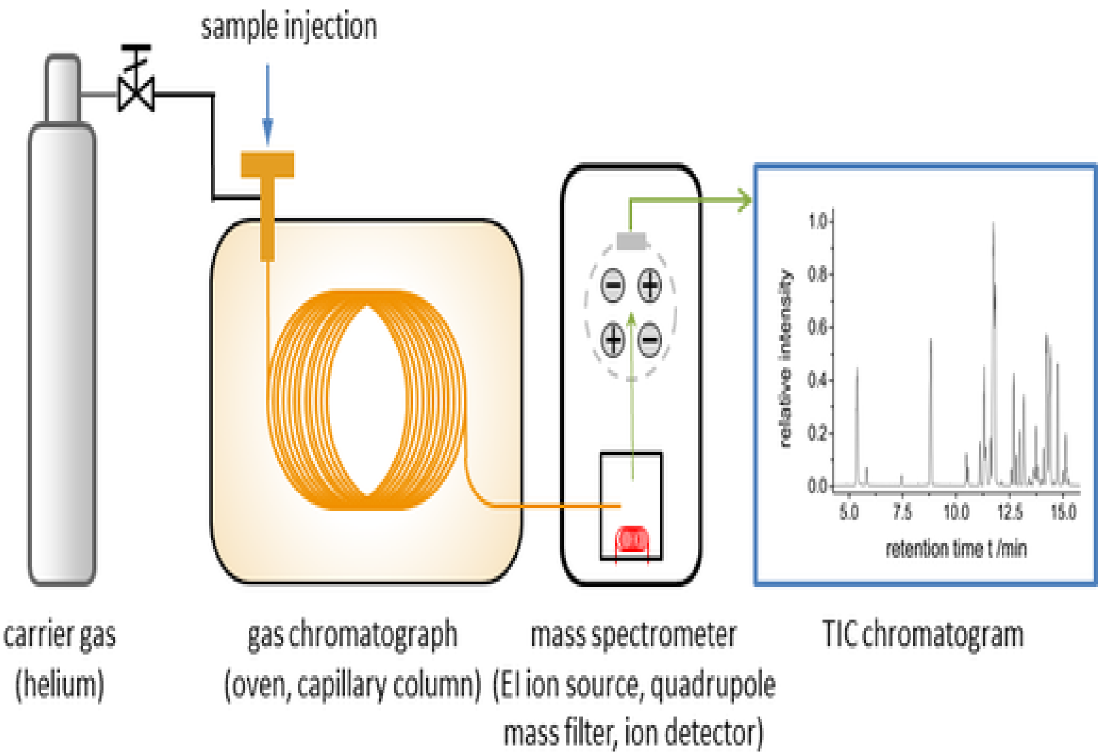

Figure 17, GC-MS illustration

The chemical composition of organic liquid product (OLP) was determined by gas chromatography–mass spectrometry (GC–MS) with the set-up shown in Figure 17. GS-MS analyses were performed on the apparatus GCMS-QP 2010 Ultra by Shimadzu. Only compounds with a probability match equal to or higher than 90% were considered best fit from the NIST Mass Spectral library. Identification of major aromatic products of petrochemical interest was confirmed based on a standard mixture containing ethylbenzene, benzene, toluene, and xylene used to pre-calibrate the GC-MS. The capillary column was a 30m× 0.25mm× 0.25 µm DB-5MS column. The GC–MS test parameters were as follows, one microliter solution was introduced through an injection port operated in a split mode with injector and detector temperature set at a constant value of 250 °C. Helium at the flow rate 0.9 ml min^{-1} was used as the carrier gas with a split ratio of 70. For the first five minutes the temperature regime of the column was isothermal at 50 °C, then the temperature increased with the gradient of 4 °C.min^{-1} up to 280 °C.

Chapter 4

4 Results and Discussion

This chapter discusses the results obtained from the characterisation and test activity of the synthesised catalyst over various ethanol-waste cooking oil mixtures. The mixtures to be converted varied from 25%, 50%, 75% and 100% WCO with the make up being the contribution of ethanol. The sections to follow falls under two major categories, characterisation of catalyst and test activity.

4.1 Characterisation of the catalysts

4.1.1 X-ray diffraction XRD

The XRD patterns of the synthesised catalysts obtained confirm high relative crystallinity of the samples even in comparison with a commercial catalyst depicted in Figure 18 with corresponding value of intensity shown in Table 2. The intensity of the important peaks of the MFI phase structure was used as a yardstick to determine relative crystallinity. The relative crystallinity was determined for the peaks at about the following 2θ range values (7°-9° and 23°- 25°) of interest for the zeolite ZSM-5 using a highly crystalline ZSM-5 sample as reference. The analysis of the data obtained is represented in Table 2 and Figure 18 in the section to follow with the synthesised HZSM-5 having the highest relative crystallinity (reference sample) in comparison to the doped catalyst system as well as the commercial catalyst.

The XRD patterns of all catalysts prepared showed the presence of the MFI phase with peaks observed at 2θ ranges of 7°- 9°and 23°- 25° as shown in Figure 18. The commercial catalyst had the lowest relative crystallinity of 86% while introduction of the metal iron and nickel lowered the relative crystallinity to values of 88 and 90% respectively. The relative crystallinity of the products was determined by comparing the sum of the peak areas at 2θ ranges of 7°- 9°and 23°- 25° with that of a well-crystallized sample (parent synthesised HZSM-5). XRD analysis done shown in Figure 18 compares the three synthesised samples used in the study, for comparison commercial HZSM-5 was also used to confirm the match in diffractogram pattern. Based on data obtained from the collection of simulated XRD powder patterns for zeolites the miller indices (hkl) and multiplicity were determined with the value of hkl shown in Table 2 below with these values confirming the monoclinic and orthorhombic crystal structure existence (Treacy and Higgins 2007).

Table 2, Relative crystallinity data and miller indices derived from XRD patterns

	2theta approximate values				
	~8°	**~9°**	**~23°**	**~24°**	
Sample ID	**Intensity (Counts)**				**Relative crystallinity**
Commercial HZSM-5	12036	6818	16135	7727	**86%**
HZSM-5	15761	7723	18369	8281	**100%**
FeHZSM-5	14285	7329	14894	7092	**88%**
NiHZSM-5	14364	6767	15670	7835	**90%**
Miller indices (hkl)	1 0 1	0 2 0	3 3 2	3 0 3	

The addition of promoters did not alter the pattern of the diffractogram with no distinct peaks that could be attributed to the metals, however the effect on relative crystallinity was observed as reported in Table 2. Low doping concentrations set as well as the ability of the zeolite to ion exchange in the framework structure may be possible reasons for the observations. However the presence of the doping metals was confirmed through elemental analysis through energy dispersive spectroscopy.

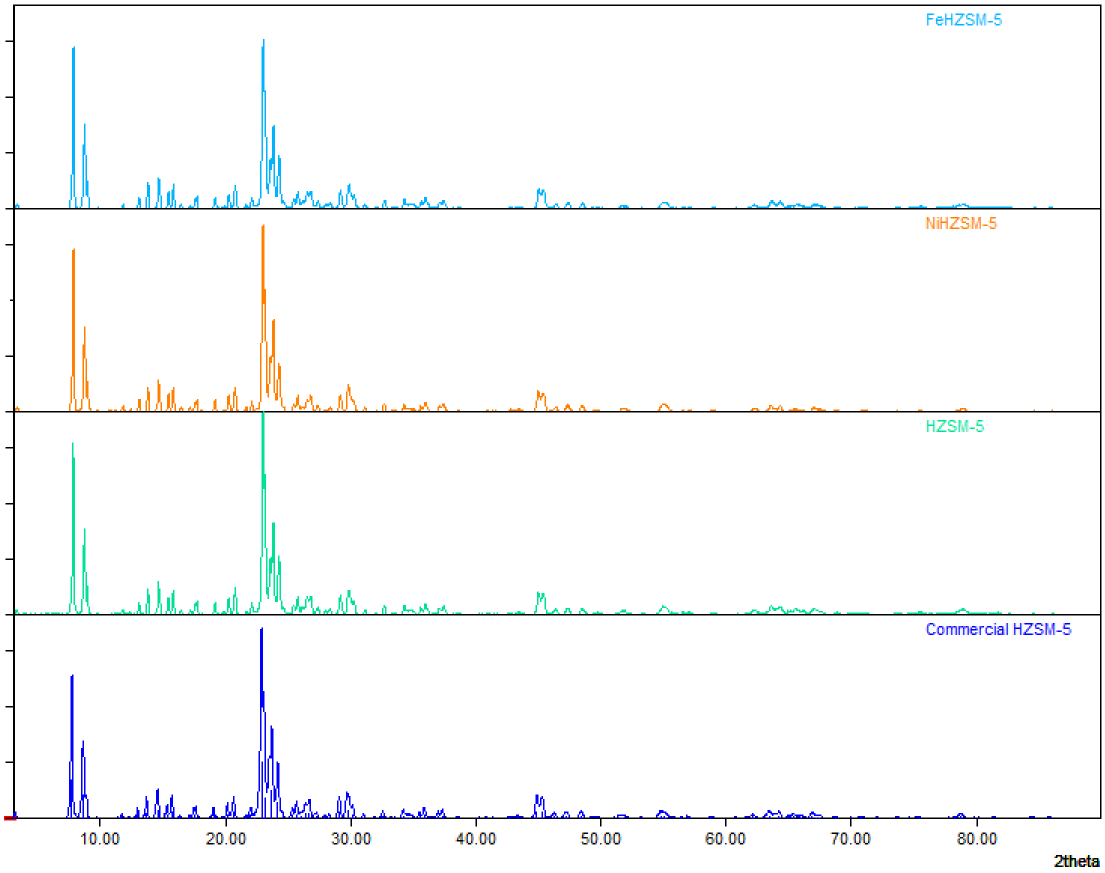

Figure 18, XRD diffractogram patterns for the catalyst

4.1.2 Energy Dispersive Spectroscopy - Scanning Electron Microscopy

Energy dispersive spectroscopy was used to give an idea the elemental composition of the synthesised material. Conclusion drawn from the analysis show that the Si/Al ratio achieved for the study was 38 lower than the initial target ratio set at the beginning of 50, with the presence of the metal promoters confirmed as shown in Table 3.

Table 3, Elemental composition from EDS analysis done with carbon coating

	C	**O**	**Al**	**Si**	**Fe**	**Ni**	**Si/Al**
HZSM-5	15.80	50.16	0.87	33.18			38.13
FeHZSM-5	21.65	46.66	0.81	30.07	1.24		37.12
NiHZSM-5	11.76	50.43	0.67	33.84		2.28	50.51

In the case of the impregnated catalysts both materials present also a comparable metal content, although slightly lower than the theoretical value (5 wt.%). One has to be careful that the doping does not result in replacement of the protons (H^+) of the zeolite as this could affect subsequent cracking reactions that include hydrogen transfer reaction, oligomerisation and cyclisation (Galadima and Muraza 2015b). The lower Si/Al ratio of 38 compared to the target ratio of synthesis resulted in increased acidity thus cracking was enhanced as highlighted by Emori *et al.* (2016) leading to increased gaseous products. The carbon content shown in Table 3 is derived from the technique employed in analysis of using carbon for coating purposes.

The major difference in the Si/Al ratio of the NiHZSM-5 catalyst compared to the parent and FeHZSM-5 shows the lower degree of accuracy of the technique use. This may be neglected as the catalyst systems used in the study were promoted from the same parent catalyst synthesised HZSM-5. The FeHZSM-5 catalyst close proximity to the parent catalyst proves that, for future lines of work the EDS analysis may not be the most ideal technique to determine the Si/Al ratio as its dependent on the average values of snaps taken at different angles. The flaw of the technique come from the fact that if one of the snaps has higher or lower values it affects the results obtained.

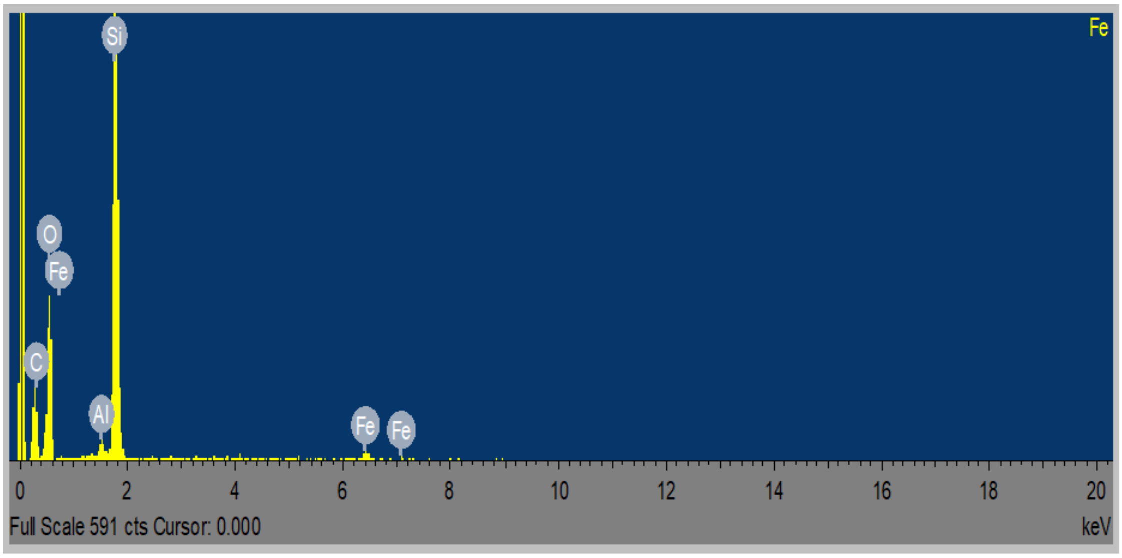

Figure 19, Fe-HZSM-5 elemental analysis

Figure 19 is an elemental analysis graph from the energy dispersive spectroscopy analysis showing the presence of iron in the FeHZSM-5 samples prepared. The choice of doping technique chosen does have an influence on the deposition of metals, with inappropriate deposits insides zeolite channels possibly causing rapid catalyst deactivation due to diffusion restrictions (Galadima and Muraza 2015b).

The scanning electron microscope (SEM) was used to identify the morphology of the synthesised catalytic material. The SEM micrographs obtained indicated that the ZSM-5 samples consist of agglomerated, inter-grown layered particles as shown in the micrograph in Figure 20 observed at a magnification X10000, with all three samples represented as HZSM-5 (parent catalyst), Ni-HZSM-5 and Fe-HZSM-5.

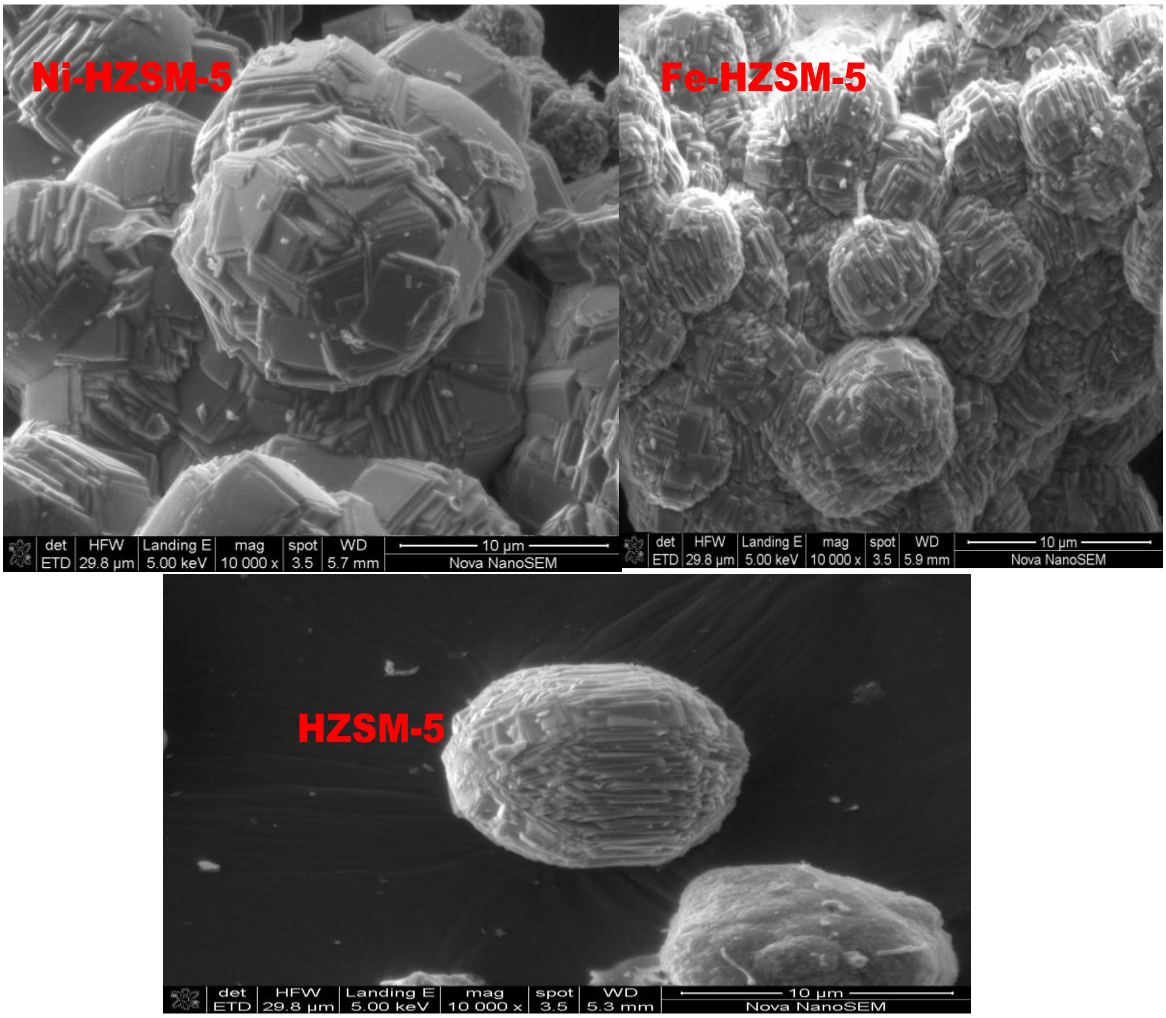

Figure 20, SEM micrographs at magnification X10 000

4.1.3 BET analyses

The agglomerated inter-grown layered particles shown in Figure 22 possess lower external surface area compared to the micropore area, with the parent synthesised catalyst having an external surface area of 83 m^2/g compared to 195 m^2/g micropore area. This may have a significant impact on the product selectivity with shape selective features of the catalyst more pronounced in the presence of higher micropore area. The decrease in surface area shown in Table 4 as a result of nickel promotion suggests that the dispersion of metal might have been on the external surface creating partial cover of part of the active sites located on the external surface. Metal etching might have contributed to the slight increase in micropore volume due to the introduction of nickel with an increase from 0.084 to 0.087 cm^3/g, as shown in Table 4.

The ideal situation would be to have the metal site present within the microporous channels to aid aromatisation by dehydrogenating the hydrocarbon molecules. The micropore volume also decreased, suggesting the occurrence of partial blocking of the channels of the zeolite and/or a limited destruction of the porous structure. High loading of metal promoters may partially block the access to the microporous network where active sites are located resulting in reduced activity and selectivity (Galadima and Muraza 2015b). Doping with the metal promoter had contrasting effects with nickel addition lowering the external surface area, from 83 m^2/g to 57 m^2/g while Fe doping had the opposite influence increasing the external surface area to 100 m^2/g. The micropore area increased with the introduction of metal promoters with FeHZSM-5 showing a notable change increasing from 195 m^2/g to 212 m^2/g and the increasing trend was also noticeable for micropore volume following the same pattern as shown in Table 4 below. The analysis based on the t-plot method show that the prepared catalysts system had surface areas of over 250 m^2/g for all catalyst systems used as well as pore volume ranging from 0.084 to just above 0.090.

Ideally, the introduction of metals to molecular sieve catalysts such as zeolites is expected to lower both the surface area and pore volume as the metals occupy the microporous network.

However, analysis done showed that only NiHZSM-5 behaved as expected in terms of surface area reduction. For FeHZSM-5, an increase in surface area was witnessed along with increased microporous volume. Possible reason for this may be due to metal nitrates introduced itching some of the microporous veins thus the volume increased. Iron metal promotion increased the external surface as well as the microporous surface area suggesting that the level of dispersion was smooth on the surface of the zeolite. The formation of metal agglomerates on the surfaces of the zeolites may result in increased surface area compared to the parent catalyst, although the analysis done did not provide conclusive evidence. The increase in surface area may not have the expected positive influence on the co-cracking process as initial interaction of long chains with externally located strong acid sites is significantly reduced (Galadima and Muraza 2015b).

Table 4, BET Analysis

t-plot report	**HZSM-5**	**NiHZSM-5**	**Fe HZSM-5**
micropore volume (cm^3/g)	0.0845	0.0875	0.0908
micropore area (m^2/g)	195.96	198.52	212.51
External surface area (m^2/g)	83.91	57.23	100.82
Total surface area (m^2/g)	279.87	255.75	313.33
Single point surface area at P/P$_o$ (m^2/g)	269.79	248.25	302.22

4.2 Catalyst testing

Analysis of waste cooking oil as shown in Table 5 below shows that more than 50% was mono-unsaturated free fatty acid in the form of oleic acid, with major contributions for the remainder occupied by mono and diglycerides (esters). In the study done by Shimada *et al.* (2016) with triglycerides the presence of unsaturated fatty acid increased the ease of deoxygenation and decomposition to organic liquid product in comparison to saturated fatty acid derivatives (Doronin *et al.* 2014; Shimada *et al.* 2016). From Table 5 below it can be seen that the waste cooking oil feedstock had a higher degree of unsaturated fatty acid derivatives (Oleic acid with 51.44% composition based on GC-MS analysis) which will have a significant influence on the ease of cracking.

Table 5, Composition of the waste cooking oil as per GC-MS analysis

Component ID	**Quantity %**
l-(+)-Ascorbic acid 2,6-dihexadecanoate (ester)	23.55
Octadec-9-enoic acid (Oleic Acid **C** 18:1)	51.44
Octadecanoic acid (Stearic acid **C** 18:0)	3.67
Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester	4.6
Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester	11.01
Ethanol	3.24
Other derivatives	2.49

4.2.1 Effect of feedstock composition on organic liquid product yield

Test activity done with the synthesised catalyst yielded high conversion of over 93% for all samples with Ni-ZSM-5 performing relatively better with over 96% conversion for all test runs done. Despite the high conversion as shown in Figure 21, the level of deoxygenation was much lower for FeHZSM-5 (25%WCO) at 400 °C and NiHZSM-5 (75%WCO) with about 20% oxygenated hydrocarbon compounds as shown in Table 6. The absence of triglyceride and fatty acid derivatives originally detected in the feedstock was used as a measure of determining the extent of the conversion making use of equation 1 shown below. The components to take note of are the triglycerides derivative and ethanol found in feedstock as a measure of the transformation.

$$Conversion\ (\%) = \frac{sum\ of\ components\ in\ feed - sum\ of\ components\ in\ liquid\ product}{sum\ \ of components\ in\ feeds} \ldots \text{equation 1}$$

Taking sample E26 shown in the appendix for sample calculations, the starting material made up mostly of triglycerides derivatives is converted to a wide range of aromatic derivatives shown in Table 8 (refer to appendix). The components in the product to contribute to the unconverted feedstock include ethanol, and triglycerides derivative found in both the feedstock and product. The results of conversion for the various runs carried out are shown in Table 6. Despite the high values of conversion recorded some of the products were found to be oxygenated hydrocarbon (as can be seen by compounds with the hydroxyl group in Table 8).

$$Conversion\ (\%) = \frac{100 - (0.45 + 0.75 + 0.50)}{100}$$

= **98.3 %**

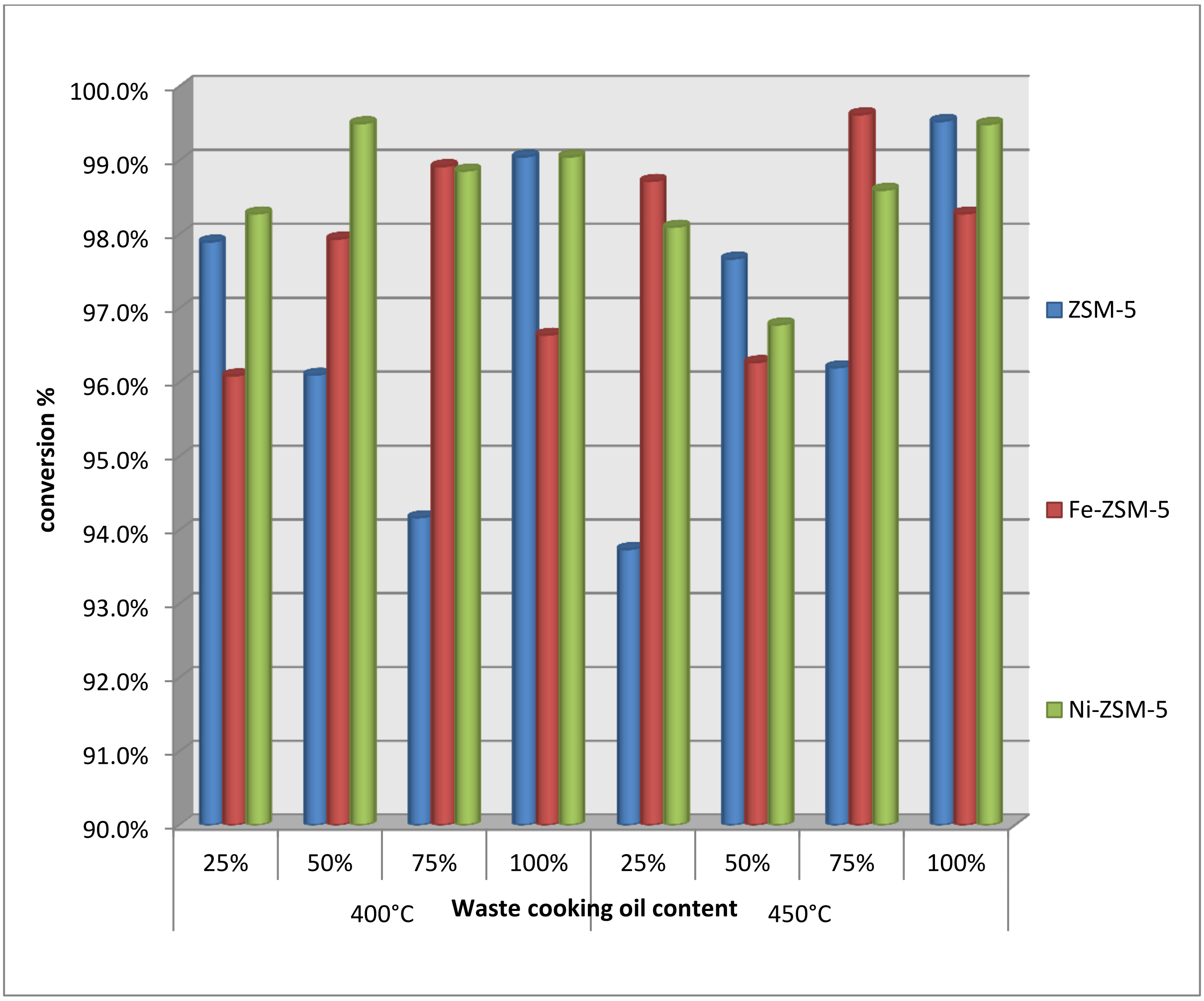

Figure 21, Conversion of Eth-WCO mixtures

The feed composition of the mixture had very little influence on the conversion. however liquid product selectivity rich in aromatics witnessed an almost linear increase as the portion of WCO in the mixture was increasing as shown in Table 6. The highest conversion of Eth-WCO mixture recorded was 99.6 % over NiZSM-5 at a reactor temperature setting of 400 °C as shown in Figure 21 conversion with a 50:50 component feed contribution of ethanol and WCO. The lowest conversion was achieved over the parent ZSM-5 catalyst yielding a value of 93.7 % at a temperature setting of 450 °C. The degree of deoxygenation correlating the weight of oxygenates in the product with reagent was used as a measure of the extent of reaction and suitability of application of product as fuel and chemical feedstocks. Incomplete deoxygenation may be due to deactivation of active site or complicated secondary reactions.

The conversion process also yielded gaseous hydrocarbon and although it was not analysed qualitatively, total gas flow rates were determined as shown in Table 6. At lower temperature settings the ZSM-5 parent catalyst and Fe-ZSM-5 produced lower gas volumes as witnessed by the lower total gas flow rates. For parent ZSM-5 with 100 % WCO total gas volume recorded was 778 ml and 2534 ml, with FeHZSM-5 recording 2131 ml and 2710 ml and NiHZSM-5 having values of 3754 ml and 4068 ml corresponding to 400 °C and 450 °C respectively as shown in Table 6.

The high conversion values are within the range obtained from a study by Teixeira *et al.* (2016) with Jatropha oil as well as a highly aromatic product distribution composed of toluene, ethyl benzene, p-xylene and naphthalene. Botas *et al.* (2014); Wang *et al.* (2015), Ahmad *et al.* (2016) stress the importance of the strong Bronsted acid sites of ZSM-5 in cracking, highlighting that addition of metal sites has a diluting effect with the metals enhancing hydrogen transfer reactions leading to high aromatic yields.

Table 6, Product distribution in the organic liquid product

		ZSM-5							
		400°C				450°C			
WCO quantity		25%	50%	75%	100%	25%	50%	75%	100%
Class ID	E15-raw	E23	E1	E2	E21	E5	E12	E16	E8
Aromatics		65.8	78.43	68.19	73.28	56.68	40.58	30.2	58.28
Polyclicaromatic		26.4	13.3	19.66	17.27	34.94	53.66	56.22	38.87
Oxygenates	100	7.24	7.92	10.88	5.2	7.93	5.76	13.58	2.85
cycloakene			0.35	0.36	0.5				
alkane		0.56		0.91	3.75	0.45			
Oil (ml)		0.7	1.3	1.5	2.5	0.5	0.7	1	1.9
Water (ml)		0.5	0.7	0.6	0	0.8	0.3	0.5	0
OLP yield %		**14%**	**26%**	**30%**	**50%**	**10%**	**14%**	**20%**	**38%**
Conversion		**97.9%**	**96.1%**	**94.2%**	**99.1%**	**93.7%**	**97.7%**	**96.2%**	**99.5%**
Total gas flow rate ml		**1589**	**955**	**1046**	**778**	**2342**	**2496**	**2676**	**2534**
Class ID	**FeHZSM-5**								
	E15-raw	E3	E14	E11	E20	E22	E9	E18	E26
Aromatics		33.72	76.63	64.78	72.46	56.35	73.66	40.2	68.81
Polyclic aromatic		46.78	13.25	26.05	15.45	37.15	17.44	50.54	23.72
Oxygenates	100	19.5	6.58	8.6	7.04	6.5	8.29	8.47	7.47
cycloakene			2.48	0.57	2.54		0.61		
alkane			1.06	0.86	2.51			0.79	
Oil (ml)		0.8	1.4	1.7	2	0.3	0.8	1.1	1.5
Water (ml)		1.3	0.5	0.3	0	0.5	0.4	0.3	0
OLP yield %		**16%**	**28%**	**34%**	**40%**	**6%**	**16%**	**22%**	**30%**
Conversion		**96.1%**	**97.9%**	**98.9%**	**96.6%**	**98.7%**	**96.3%**	**99.6%**	**98.3%**
Total gas flow rate ml		**1312**	**1548**	**2316**	**2131**	**2866**	**3041**	**3132**	**2710**
Class ID	**NiHZSM-5**								
	E15-raw	E4	E24	E17	E10	E7	E13	E19	E25
Aromatics		59.43	57.87	69.64	49.24	65.1	14.95	19.62	57.94
Polyclic aromatic		35.33	30.96	26.74	49.81	22.77	75.72	60.6	33.96
Oxygenates	100	4.8	8.71	3.62	0.95	10.66	9.33	19.33	8.1
cycloakene			1.8			0.64			
alkane		0.44	0.66			0.83		0.45	
Oil (ml)		0.6	0.8	1.6	2.2	0.4	0.6	0.9	1.8
Water (ml)		1.1	0.5	0.2	0	0.8	0.2	0.2	0
OLP yield %		**12%**	**16%**	**32%**	**44%**	**8%**	**12%**	**18%**	**36%**
Conversion		**98.3%**	**99.5%**	**98.9%**	**99.1%**	**98.1%**	**96.8%**	**98.6%**	**99.5%**
Total gas flow rate ml		**2297**	**3259**	**3118**	**3754**	**3206**	**4219**	**3571**	**4068**

The trend followed the general pattern for of increasing with the introduction of metals in the order of FeHZSM-5 before NiHZSM-5 in term of volume of gas produced except for sample with parent catalyst at 400 °C with 25 % WCO where the lowest volume was produced by iron promoted catalyst. NiHZSM-5's high yields could be attributed to its strong potential to dehydrogenate molecules leaving them highly susceptible to secondary reactions such as cracking. With increasing temperature setting for all catalysts there was a general increase in the volumetric gas flow rate produced showing that secondary cracking reaction are highly favoured by thermal effect resulting in increased production of lighter gases.

The organic liquid yield decreased with increasing temperature across the three catalyst systems with the highest yield obtained over parent catalyst systems with a high value of 50% observed with pure waste cooking oil feed. Observations made for pure waste cooking oil feed across the test activity was that no water was present in the liquid product collected which may point to deoxygenation via decarboxylation/decarbonylation pathways explained in the study by Shimada *et al.* (2016). The small yields of water present in the liquid product collected for ethanol containing mixtures could be attributed to the prominence of dehydration for ethanol upgrade over acidic solid catalyst to form olefins which are upgraded through oligomerisation, cyclisation, and aromatisation to gasoline range hydrocarbons. Taking sample E12 which is a 50%WCO: 50%Eth, sample calculation are shown below based on the liquid sample products collected in 5 ml vials. The sample had two distinct phases, an aqueous water phase as well as the organic liquid products. The yield was determined based on the organic liquid product and more data is presented in Table 6.

$$Yield\ of\ OLP\ (wt.\%) = \frac{volume\ of\ liquid\ product\ (ml)}{volume\ of\ feed\ mixture(ml)} \quad \text{..equation 2}$$

$$Yield\ of\ OLP\ (wt.\%) = \frac{0.7}{5}$$

= **14**%

It was observed that the increased contribution of waste cooking oil in the mixture had a linearly contribution to the formation of liquid organic product increase as the content in the mixture was altered across all catalysts used. For the qualitative characterisation of the organic liquid product a distinction was made between the aromatic hydrocarbons produced with the monoaromatics to be referred to as aromatics in the study with polyaromatics assigned to the double ringed aromatics such as naphthalene and their derivatives.

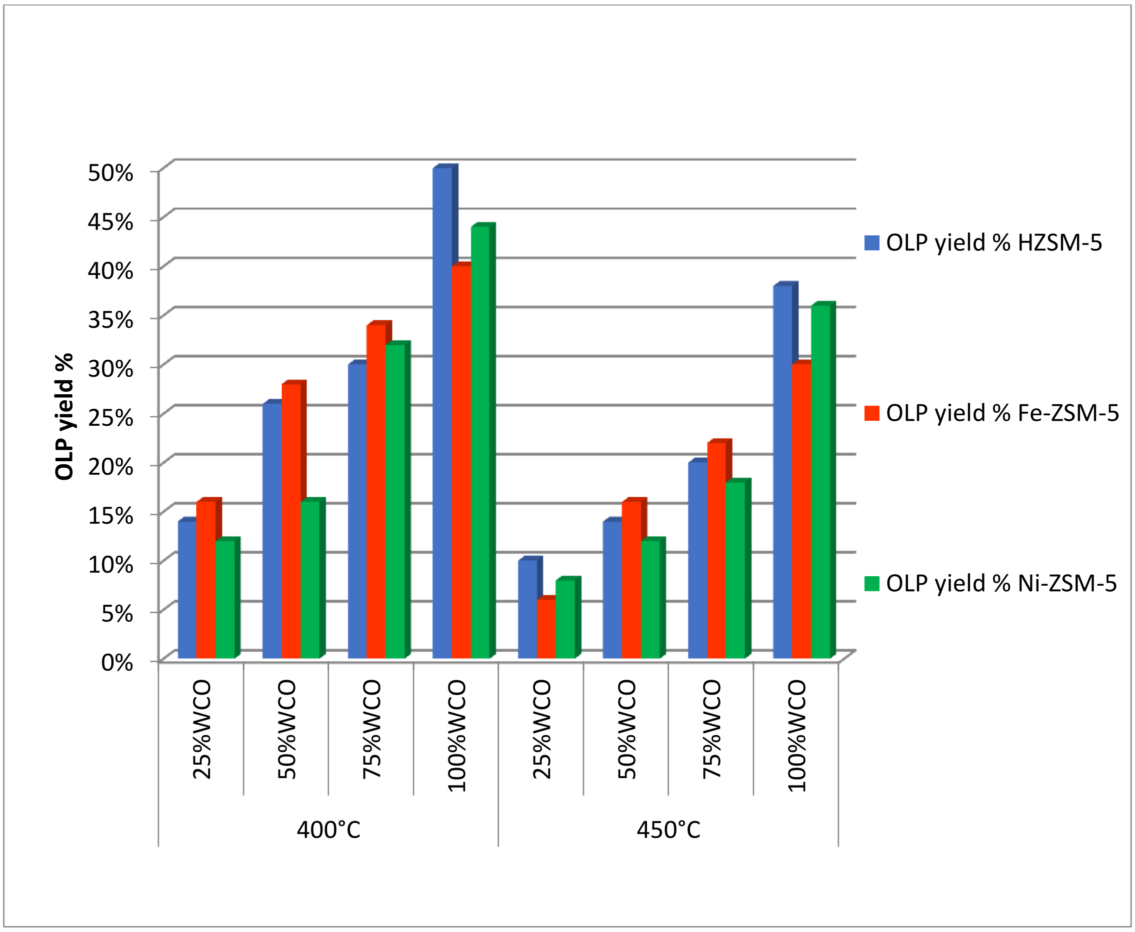

Figure 22, Organic liquid output yield for the different catalysts system

Focus on calculations was placed on organic liquid product output taking into account the amount of feedstock fed, which meant the gaseous hydrocarbons were not considered due to limitations placed on the study. The liquid hydrocarbon yield for the different catalyst systems employed as shown in Figure 22 highlights that with an increase in the triglyceride content of the feed, there was a corresponding increase in organic liquid product output.

Doping with metals lowered the organic liquid yield in comparison to the parent catalyst systems which can be linked to the influence of Bronsted acid sites which are reduced upon the introduction of metal sites (Ahmad *et al.* 2016). The metal sites introduction reduced quantity of strong Brønsted acid sites which support aromatisation of the intermediate hydrocarbon thus lowering the yield of the liquid product a suggested by Botas *et al.* (2014); Ahmad *et al.* (2016). An increase in temperature from 400 to 450 °C resulted in a decrease of the liquid output from the reactor as more gas product was produced from the process with increased secondary reactions (cracking to lower molecular weight hydrocarbons) expected to occur at higher temperatures. Introduction of a doping agent in the form of metals nickel and iron did not improve the overall hydrocarbon yield compared to the parent catalyst material with slightly lower yields following the same trend for the increasing in triglyceride (WCO) content of the feed.

4.2.2 Effect of doping synthesised HZSM-5 catalyst with metals (Fe and Ni)

The dehydrogenation ability of the metal promoter allows for feedstock hydrogen to be available for deoxygenation of triglyceride suppressing carbon loss in the conversion process through decarboxylation, with increased aqueous phase in the liquid product according to the mechanism suggested by Shimada *et al.* (2016). It is imperative that a balance is struck between weakening the density of the strong acid sites responsible for highly valuable secondary reactions with the increase in density of weak acid site to catalyse dehydrogenation reaction as mentioned in the study by Ahmad *et al.* (2016). Doping with iron yielded some notable cycloalkane (naphthenic) products as shown in Figure 23, in small amounts at the temperature of 400 °C showing the influence of metallic acid sites in lowering the density of Bronsted acid sites responsible for hydride transfer reactions leading to cyclisation and aromatisation. Poly aromatic yields under the influence of iron doping were significantly lower compared to the parent catalyst as well as the nickel doped systems.

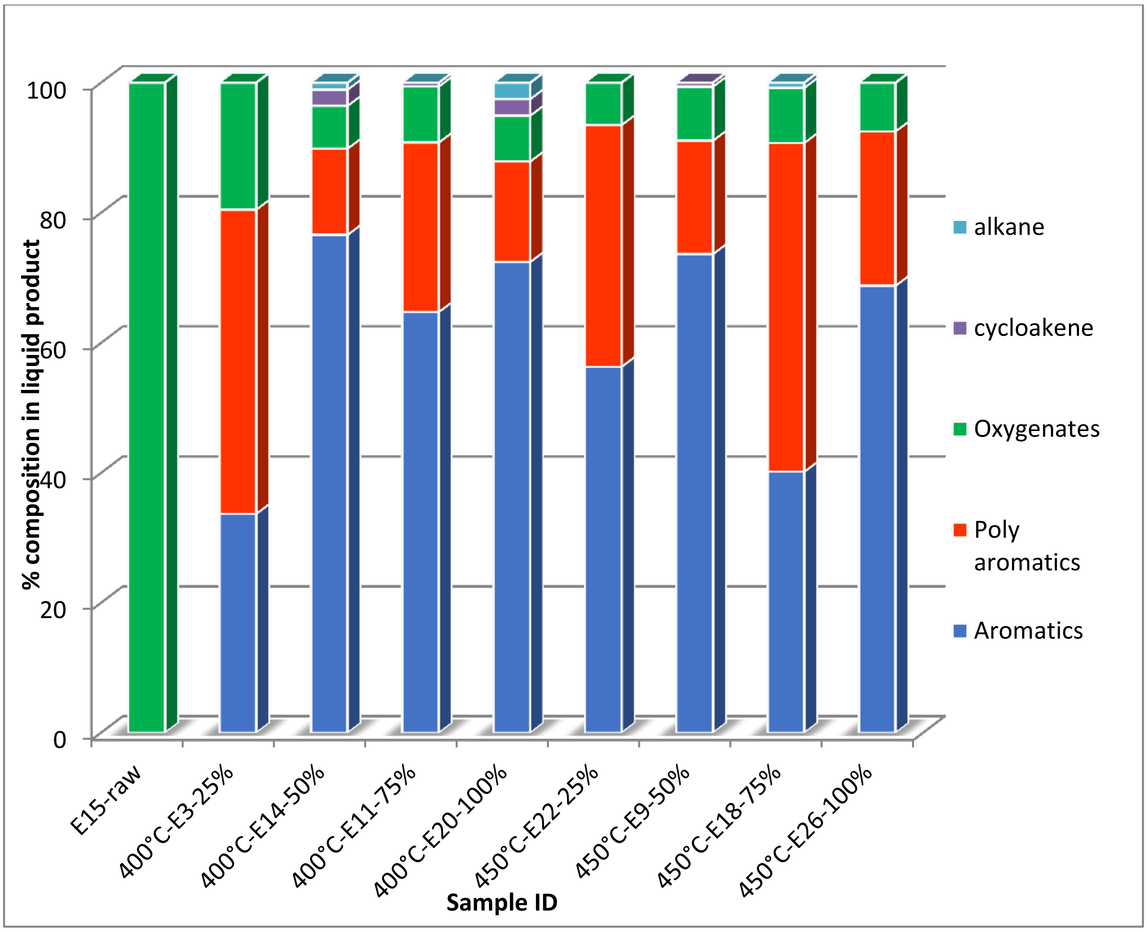

Figure 23, Performance of iron promoted FeHZSM-5 catalyst over ETH- WCO mixtures

Nickel doped catalyst systems produced high poly aromatic compounds at higher temperature setting of 450 °C going as high as 75% as shown in Figure 24 for an 50Eth;50WCO weight mixture with sample ID 450°C-E9-50% (where 450 °C is the temperature, E9 is the experimental run and 50% is the contribution of WCO to the mixture). The observed trend with nickel doped catalyst system can be attributed to its high hydrogenating power in comparison to iron which aids in hydrogen transfer reactions leading to aromatic formation and subsequently poly aromatisation with increased Lewis acid sites contribution from the metal addition. The increased rate of poly aromatisation for both metal doped catalyst systems led to lower yields of the organic liquid product as they are expected to contribute to catalyst activity loss as a result of coke formation from the poly aromatic compounds. Small yields of saturated alkanes were observed in different catalyst systems with the highest selectivity witnessed for pure waste cooking oil feed at 400 °C with a value of 3.75%. However, in general the aromaticity level was high throughout the tested mixtures as expected over acid zeolite ZSM-5.

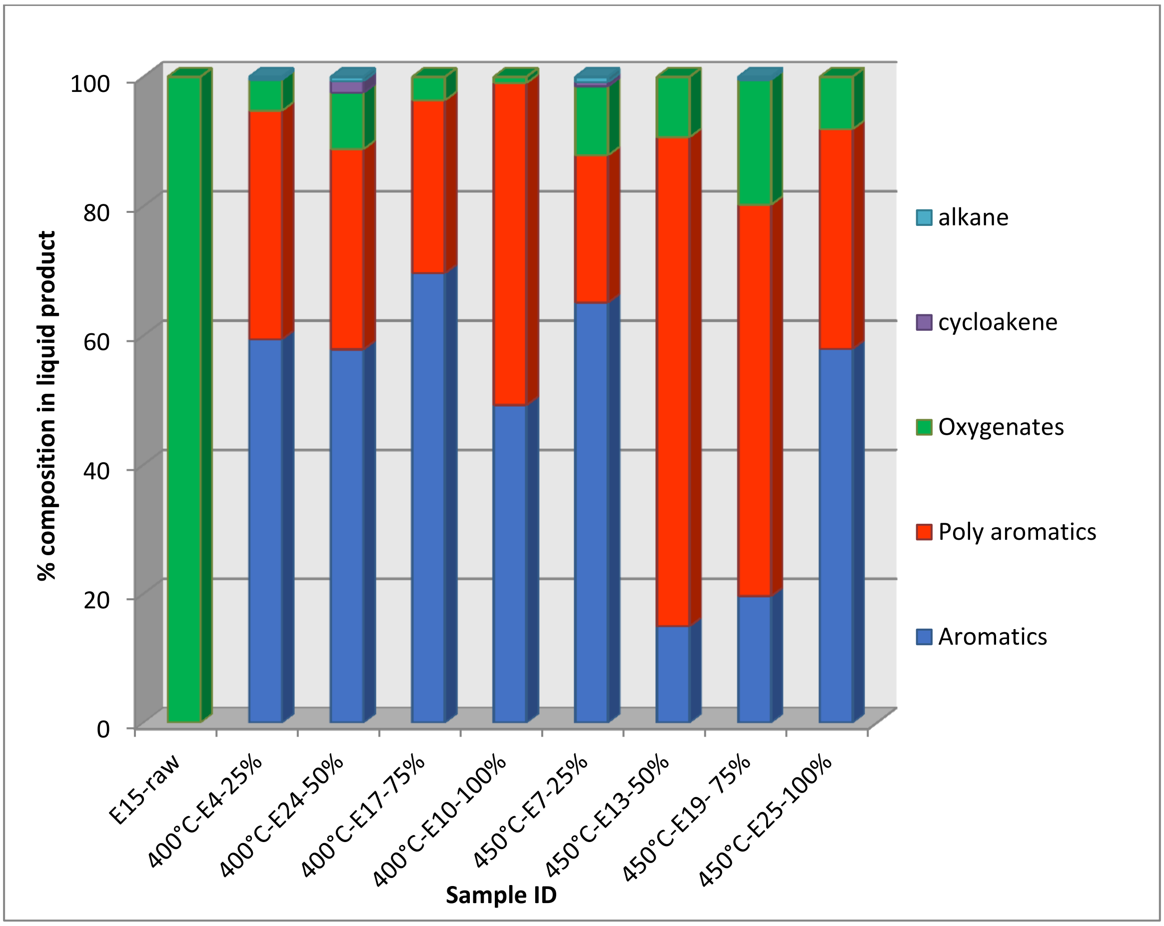

Figure 24, Performance of nickel promoted ZSM-5 catalyst over ETH-WCO mixtures

4.2.3 Effect of temperature change on the Eth-WCO mixture conversion

The influence of temperature on the extent of secondary reactions cannot be ignored, with the rate of decomposition expected to increase with an increase in temperature. From the experiments conducted in the current study less organic liquid product was obtained with an incremental change of 50 °C from 400 °C and it is expected that the yield of shorter chain lower hydrocarbons (alkanes and alkenes) should increase lowering the quantity of the organic liquid product. At higher temperatures the highly reactive nature of olefins intermediates of ethanol dehydration and cracking of triglycerides participate in hydride transfer reactions leading to the formation of coke precursors in the form of polyaromatics which may ultimately lead to coke formation resulting in loss of activity. With increase in temperature the propensity for coke precursors also increased leading to lower organic liquid yields observed at temperatures of 450 °C as well as increased selectivity to naphthalene derivatives. Deoxygenation pathways have also been made to be temperature dependent with higher temperature leading to decarboxylation while lower temperatures leaned towards decarbonylation. Decarboxylation is preferred as per every mole of carbon lost two oxygen molecules are removed in the process leading to better effective hydrogen to carbon ratio which can be used as a measure of the fuel potential of the product (Shimada *et al.* 2016).

At lower temperature deoxygenation levels were low as seen in Table 6 by high oxygenate hydrocarbon levels in the organic liquid product confirmed through GC-MS analysis for samples E19 and E3 with close to 20% oxygenates in the organic liquid product. Increased temperatures despite favouring deoxygenation also enhanced cracking activity resulting in more of the gaseous product however characterisation was limited to the liquid product. The performance of the parent catalyst systems showed that at 400 °C the content of mono aromatics was high compared to poly-aromatics which were more abundant at 450 °C. Secondary reactions which are responsible for the transformation to deoxygenated hydrocarbons from the fatty acids can be seen to be thermo-catalytic dependent with the presence of alkanes and cycloalkenes witnessed for the lower temperatures as shown in Figure 25. The influence of temperature on the formation of poly-aromatics with values over 50% found at 450 °C for mixture with 75% and 100% WCO in agreement with literature sources that point to high temperature causing poly-aromatic precursor which may lead to deactivation through coke formation.

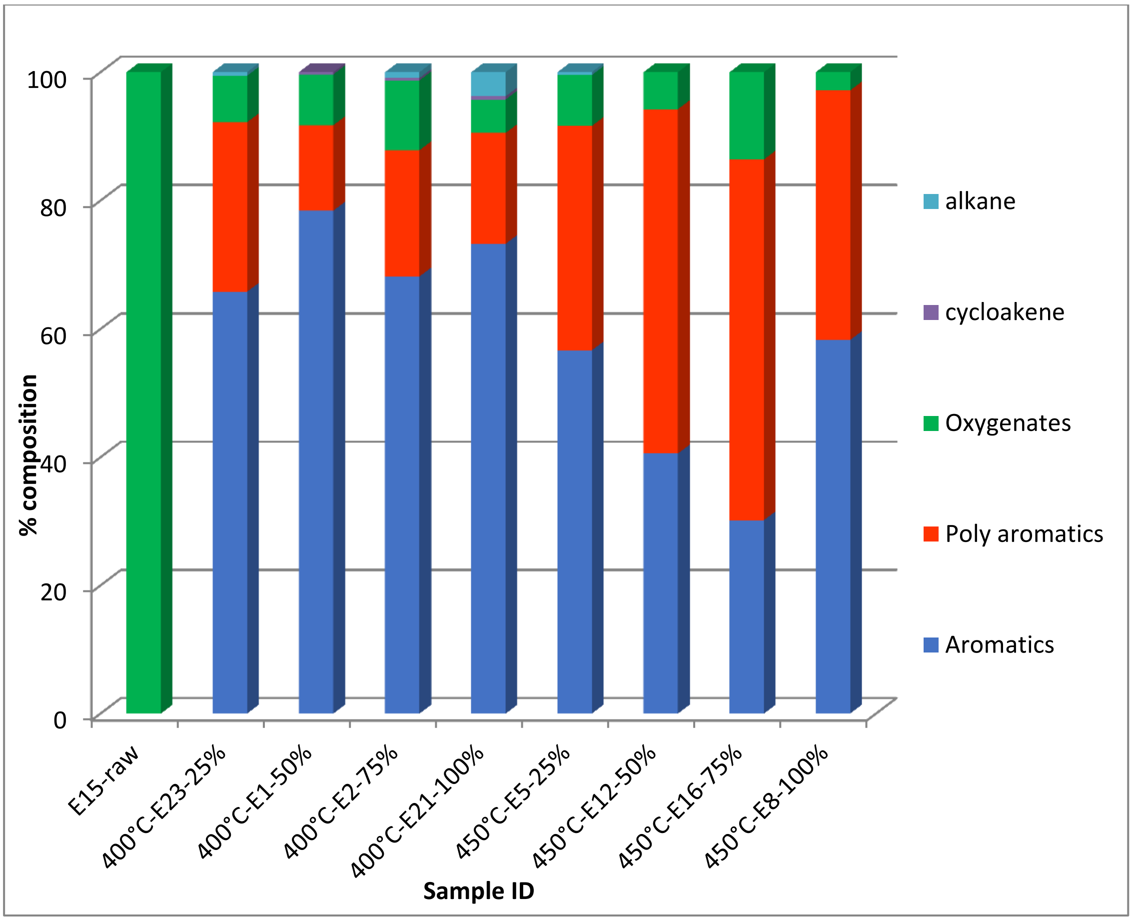

Figure 25, Performance of parent HZSM-5 catalyst system over ETH-WCO mixtures

The Figure 25 shows that the parent catalyst system produced more of the mono-aromatic hydrocarbon typical of shape selectivity of the ZSM-5 zeolite as well as high acidity. The lower content of the poly-aromatic hydrocarbons in contrast to the nickel doped catalyst system shows the influence of increasing Lewis acid site (in this instance associated to metal site) which influence the dehydrogenation responsible for aromatisation and hydride transfer reactions. A consequence of deactivation with time on stream saw the reduction of liquid yield and overall conversion and increased rate of production of lighter products.

4.2.4 Product classification and possible integration into fuel and chemical industry

The general trend for the product distribution highlighted the impact of the high Bronsted acid sites in furthering hydride transfer reactions leading to alkylated aromatics or cyclised aromatics such as indane, mesitylene, toluene, benzene, 1 ethyl-2-methyl.The data from the

GC-MS characterisation is shownin Tables 5 and 6 with Table 6 showing some hydrocarbons of interest such as the BTEX chemical precursors. Secondary reactions during the catalytic upgrade were influenced by shape selective feature of the catalyst employed and in the current study, the ZSM-5 high shape selectivity towards aromatics resulted in a greater selectivity for alkylated benzene derivatives mostly less than C_{11} useful as renewable sources of chemical industry feedstock. Shape selective product outputs suggest the influence of internally located active sites for secondary reactions while the naphthalene selectivity which is also high is a cause for concern with respect to catalyst activity loss through coking (Ahmad *et al.* 2016; Lam *et al.* 2016). Some of the aromatic hydrocarbons such as BTEX component in the product stream have important roles in the commodity and specialty chemical manufacturing sector consumed in very large volumes worldwide (Mo and Savage 2013; Maneffa *et al.* 2016).

Aromatics are the starting material for a wide range of consumer products, such as clothing, pharmaceuticals, cosmetics, computers, paints, vehicle components, cooking utensils, fabrics and sports equipment (Maneffa *et al.* 2016). Aromatics such as benzene-toluene-ethylbenzene-xylene (BTEX) are useful chemicals for fuels and petrochemicals with the content of benzene a carcinogen and some of the aromatics to be limited in biofuels (Maneffa *et al.* 2016). Thus, it is imperative that technologies be developed that can supply the most commonly used aromatics from alternative, renewable resources. Current production routes for such chemicals have been through catalytic reforming of naphtha in petroleum refineries (Maneffa *et al.* 2016). One such example is p-xylene a precursor for terephthalic acid production, a monomer used to make polyethylene terephthalate (PET) for the production of fibres and beverage bottles (Mo and Savage 2013; Maneffa *et al.* 2016).

The high variability in the compounds formed over the catalytic upgrade process in the current study is a cause for concern as adoption into current processing system will become extremely difficult. The presence of oxygenated hydrocarbons in the organic liquid product could suggest catalyst deactivation which may be confirmed by quantifying the coke deposits. Several studies suggest that with the introduction of metals, aromatisation is increased as hydride transfer reactions are enhanced if the metal sites possess dehydrogenation powers.

The high proportion of the microporous area might explain the highly shape selective influenced product distribution with high aromatics such as toluene, ethylbenzene and xylene. Despite the high octane rating of aromatic compounds, the required quality of fuel limits the quantity of aromatic content therefore the organic liquid product obtained from the current study would be better suited as chemical precursors for commodity and specialty chemical production.

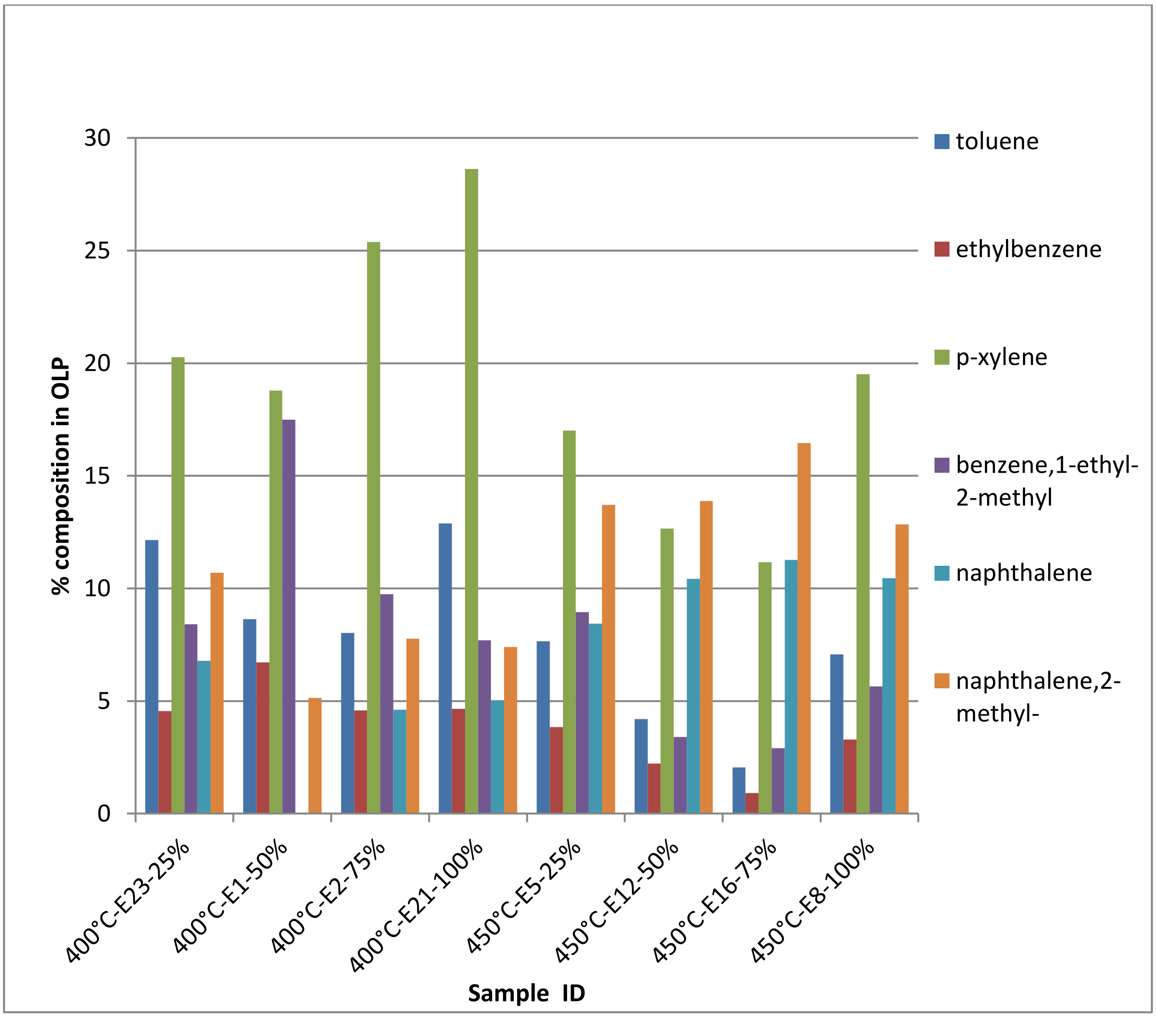

Figure 26, Influence of parent HZSM-5 catalyst on major constituents of liquid product

The parent ZSM-5 system yielded lower selectivity for p xylene an aromatic of interest shown in Figure 26 useful in the production of polyethylene terephthalate compared to iron promoted catalysts which yielded very high values above 25% selectivity as shown in Figure 27 for sample E14, E11and E20 done at 400°C. The trend observed showed that with an increase in temperature lower selectivity for products of interests was observed generally though it was not a linear increase over the different WCO ratios in the feed. From the GC-MS analysis it can be observed that some substituted aromatics such as mesitylene, indane and indene were highly favoured by the parent catalyst which shows the influence of the stronger Bronsted acid sites. Doping with metals lowered the ratio of the strong acid sites thus this led to lower levels of substituted aromatic compounds.

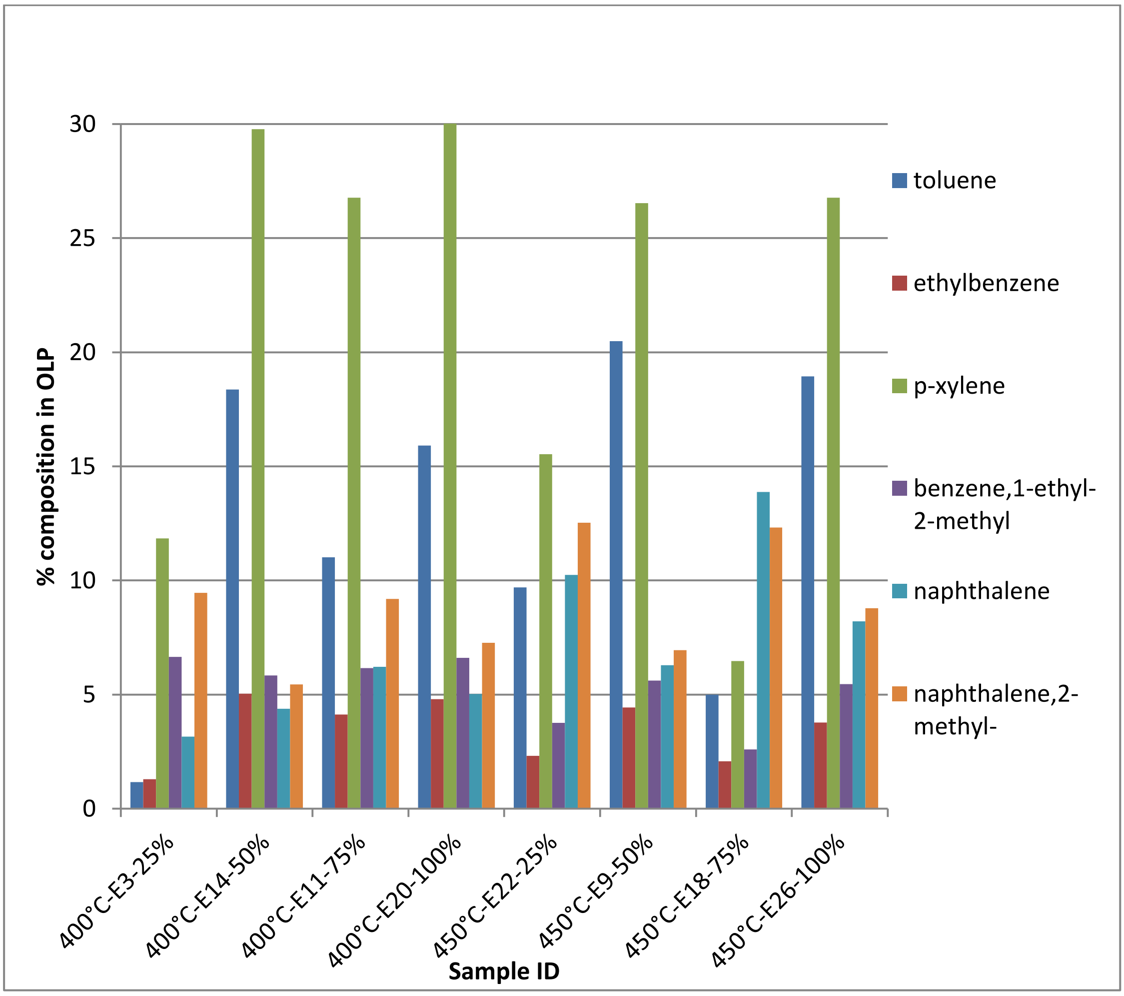

Figure 27, Influence of doping with FeHZSM-5 on major constituents of liquid product

Chapter 5

Conclusion and Recommendation

Integration of renewable carbon sources as feedstock for production of fuels and chemicals may help modern society lower their environmental footprint and reduce pressure on fossil resources. To achieve true sustainability the use of high-value feedstocks such as edible vegetable oils and sugars will need to be reduced as well as develop transformation techniques that allows for easy integration into current existing infrastructure and process of manufactures. The highly aromatic nature of the product streams obtained in this study have the potential to be part of the alternative drop-ins that may be utilised in fuel (due to high octane ratings) and chemical industry to produce commodity chemicals of high value. Commodity chemical industry is highly profitable and the use of renewable carbon sources may allow for economic benefits to the biorefinery industry which have currently been relying on subsidy and incentives to remain viable in light of lower crude oil prices.

The work done in this study looks at how integrated processing may be implemented with low cost feedstock in the form of waste cooking oil and ethanol. Ethanol a feedstock which can be derived from biomass looks to be on a promising path in terms of increased volumes of production with 2nd generation production techniques almost mature in the form of lignocellulose valorisation. The increased volumes from the biological fermentation may be integrated in co processing with triglycerides to high value chemicals and low value fuels over zeolite acid solid catalyst as proven in the study.

From the research study, the following conclusions were drawn;-

- The zeolite HZSM-5 was successfully synthesised and modified for use in the conversion of ethanol-waste cooking oil mixtures leading to the production of aromatic rich hydrocarbons that may be used as fuel and chemicals.

- Varying the feed composition (ethanol to waste cooking oil ratio) had an influence on the product distribution with pure waste cooking oil producing higher liquid product output.
- Increasing the temperature from 400 °C to 450 °C had an impact on the organic liquid product output, at 450 °C lower liquid product output was observed showing increased thermal influence led to increased cracking to lower gaseous hydrocarbons. Temperature changes influenced the extent of secondary cracking reactions and as expected with increasing temperature, the organic liquid product yield decreased.
- Catalyst properties of the synthesised material influenced by doping with promoter metals (Ni or Fe) influenced the extent of aromatisation; FeHZSM-5 produced more toluene, p-xylene hydrocarbons which may find application in fuel and petrochemical industry.

To confirm the successful synthesis of HZSM-5, diffraction patterns were analysed and compared to known MFI structure patterns. The Si/Al ratio with a direct influence on the acidity of the prepared HZSM-5 catalyst was determined from the EDS technique. The target Si/Al ratio of 50 was not obtained as per data obtained from EDS analysis, instead the ratio achieved practically was 38 which could have significant influence on the acidity of the catalyst. The high aromatisation and cracking activity might have been influenced by the high acidity of the prepared catalyst with a lower Si/Al ratio than initially set out to achieve increasing the Bronsted acid sites available. The microporous nature of the developed catalyst was determined from BET analysis and results from the study show characteristic shape selective material was produced.

Future lines of work should look at the potential of the coke deposits on the catalyst which may be in the form of carbon nano-tubes a high value product, precedence has been set in the study by Botas et al. (2014). In order to achieve better results on the deposits on the external zeolite surface that include metal dispersion and the qualitative analysis of coke (in case carbon nanotubes form), it would be recommended to do Transmission Electron Microscopy (TEM) for the fresh and used catalysts. The results of TEM analysis would better articulate if the doped zeolites performed in the same manner as in the study by (Botas et al. 2014). Limitations placed on the current study focused on the qualitative analysis of the organic liquid products. In this study, evaluation of acidity analysis was not done to investigate the influence of metal introduction on the catalyst systems and I would recommend it for future works done with multi-functional catalyst systems. However, with various studies showing that interesting gaseous products of value may be formed such as olefins for the petrochemical industry as well as possible hydrogen gas in the product. These valuable products are currently heavily reliant on refinery operations, and in the spirit of adopting renewable materials it would benefit society if future works look at the potential that lies in co-cracking of biomass feedstock for their production.

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Appendix

Table 7, Aromatics yields of significance

	ZSM-5							
	400^{o}C				450^{o}C			
WCO quantity	25%	50%	75%	100%	25%	50%	75%	100%
toluene	12.15	8.63	8.03	12.89	7.65	4.2	2.05	7.07
ethylbenzene	4.56	6.72	4.58	4.65	3.84	2.22	0.92	3.29
p-xylene	20.26	18.78	25.39	28.63	17.01	12.66	11.17	19.51
benzene,1-ethyl-2-methyl	8.41	17.49	9.75	7.69	8.95	3.4	2.9	5.65
naphthalene	6.78		4.61	5.02	8.43	10.43	11.26	10.45
naphthalene,2-methyl-	10.69	5.13	7.77	7.4	13.71	13.88	16.46	12.85
	Fe-ZSM-5							
	25%	50%	75%	100%	25%	50%	75%	100%
toluene	1.16	18.36	11.02	15.91	9.7	20.49	4.99	18.94
ethylbenzene	1.29	5.03	4.13	4.8	2.31	4.44	2.07	3.77
p-xylene	11.84	29.77	26.77	30.09	15.53	26.53	6.47	26.77
benzene,1-ethyl-2-methyl	6.65	5.83	6.16	6.61	3.76	5.61	2.59	5.46
naphthalene	3.15	4.37	6.22	5.02	10.24	6.28	13.88	8.21
naphthalene,2-methyl-	9.46	5.45	9.19	7.27	12.53	6.95	12.32	8.78
	Ni-ZSM-5							
	25%	50%	75%	100%	25%	50%	75%	100%
toluene	11.73	12.11	8.46	4.41	10.19	1.12	0.49	16.86
ethylbenzene	2.81			1.89	4.11	0.75		2.4
p-xylene	21.46	25.93	23.83	15.72	22.94	5.32	4.9	21.74
benzene,1-ethyl-2-methyl	3.57	4.48	7.63	3.56	6.29	1.25	1.14	3.28
naphthalene	8.19	6.94	6.39	11.68	6.76	8.26	8.64	9.82
naphthalene,2-methyl-	11.52	10.52	9.34	16.46	8.54	14.73	15.5	10.88

Table 8, Sample E26 GC-MS results

Sample E25 GC-MS analysis results			
Peak #	**Retention time**	**Area %**	**Component name**
1	1.602	0.45	Ethanol
2	2.453	3.50	Benzene
3	4.148	18.84	Toulene
4	6.901	3.77	Ethyl-benzene
5	8.429	26.67	p-Xylene
6	10.634	0.35	Benzene, propyl
7	11.227	5.46	Benzene,1-ethyl-2-methyl-
8	12.548	3.86	Mesitylene
9	14.130	2.01	Indane
10	14.583	2.60	1H-indene, 1-chloro-2,3-dihydro
11	14.980	0.79	Benzene,1-ethyl-3-propyl-
12	18.406	2.02	Benzene,1-methyl-2-(2-propenyl)-
13	16.176	0.74	Benzene, 1-ethyl-3,5-dimethyl
14	19.108	3.49	Naphthalene, 1,2 -dihydro-
15	19.261	0.81	Naphthalene, 1,2,3,4 -tetrahydro-
16	20.476	8.21	Naphthalene
17	23.040	0.51	1H-Indene, 1,3-dimethyl-
18	24.624	8.67	Naphthalene, 2-methyl-
19	27.792	1.17	Naphthalene, 2-ethyl-
20	28.760	3.22	Naphthalene, 1,6-dimethyl
21	28.631	0.63	Naphthalene, 1,3-dimethyl
22	30.760	0.19	Naphthalene, 1-propyl-
23	31.328	0.79	Naphthalene, 1,6,7-trimethyl-
24	39.755	0.50	Dibenzo 7.8diazabicyclo[2.2.2]octa-2,5-d
25	42.879	0.75	l-(+)-Ascorbic acid 2,6-dihexadecanoate (ester)

Table 9, Tabulated GC-MS results for ZSM-5 catalyst

Catalyst ID			**ZSM-5**							
Temperature			400°C				450°C			
WCO to ethanol content (w/w vol.)			25%	50%	75%	100%	25%	50%	75%	100%
ID	**Class**	**E15-raw**	**E23**	**E1**	**E2**	**E21**	**E5**	**E12**	**E16**	**E8**
Water	oxygenate	0.18					0.56	0.86	3.8	
Ethanol	oxygenate	3.24	0.44	0.88	0.95		1.38	0.79		0.47
Benzene	aromatic		1.27	1.48		1.53	1.26	0.12		0.19
Toluene	aromatic		12.2	8.63	8.03	12.89	7.65	4.2	2.05	7.07
Ethylbenzene	aromatic		4.56	6.72	4.58	4.65	3.84	2.22	0.92	3.29
p-xylene	aromatic		20.3	18.8	25.4	28.63	17	12.7	11.2	19.51
benzene,1-ethyl-2-methyl	aromatic		8.41	17.5	9.75	7.69	8.95	3.4	2.9	5.65
benzene,propyl	aromatic		0.66	1.36	0.94	0.86	0.71			0.55
Mesitylene	aromatic		4.35	5.64	5.14	4.23	4.69	2.03	2.35	3.19
Indane	aromatic		2.41	1.23	2.63	2.48	1.49	1.4	1.33	1.71
Indene	aromatic		1.23			0.91	1.09	2.38	2.25	2.86
benzene, 1-ethyl-3,5-dimethyl	aromatic		2.39	4.5	1.37	1	1.22			0.36
benzene,1-methyl-2-(2-propenyl)-	aromatic		2.46	2.98	4.59	1.86	2.5	1.89	1.02	1.86
2-methylindene	aromatic		2.6		2.28	2.24	3.04	3.18	1.76	3.62
Naphthalene	poly aromatic		6.78		4.61	5.02	8.43	10.4	11.3	10.45
naphthalene,2-methyl-	poly aromatic		10.7	5.13	7.77	7.4	13.7	13.9	16.5	12.85
naphthalene, 2-ethyl-	poly aromatic		1.21	1.09	0.97	0.97	1.33	2.73	2.93	2.28
naphthalene, 1,6-dimethyl	poly aromatic			3.6		2.75	2.09		4.18	3.11
naphthalene, 1,5-dimethyl	poly aromatic		4.66				2.68	3.41		
naphthalene, 1,3-dimethyl	poly aromatic		1.09	0.38	4.51	0.72	1.71	2.18	4.33	3.44
naphthalene, 1,4,6-trimethyl-	poly aromatic				1.06	0.45	1.08		1.93	
1-(+)ascorbic acid 2,6-dihexadecanoate	oxygenate	23.55	0.36		2.26		0.59			
Octadec-9-enoic acid	oxygenate	51.44					1.21			
Hexadecanoic acid, 2-hydroxy-1-	oxygenate	4.6			1.16					
9-Octadecenoic acid, 2,3-dihydroxypropyl	oxygenate	11.01								
Octadecanoic acid	oxygenate	3.67					2.52			