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Conversion of biomass-derived oil over promoted ZSM-5 based catalysts

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Declaration

I, Endifenge HAIKELA, hereby declare that this dissertation titled *Conversion of biomass-derived oil over promoted ZSM-5 based catalysts,* is work of my own toil and to the best of my knowledge, it does not contain previously published content, except where courtesy and or reference has been made. I further indicate that I have not submitted it to any other institution for the award of a degree.

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Advisor **Signature**

Abstract

Crude canola oil was thermo-catalytically converted to unsaturated hydrocarbons and aromatics. The major products were: 1,5-Heptadien-3-yne, 1,3-Hexadien-5-yne, 1-ethenyl-3-methylene-cyclopentene and Xylenes for Ni-ZSM-5, Benzene, Toluene, and other Aromatics including Ethylbenzene for Sn-ZSM-5 samples. The preparation of Ni and Sn-HZSM-5 was achieved by calcining the commercial NH_4-ZSM-5, Si/Al ratio of 50, and promoting the material with Ni and Sn chlorides. Various techniques were used to promote the catalysts, namely, mechanical mixing promotion (MM), incipient wetness promotion (IW) and aqueous promotion (AQ). All the reactions were carried out at a WHSV of 10.6 hr^{-1} and temperature of 450°C. A fixed bed reactor system was used. To understand the reactions involved in the process, the characterization of the feed was done by GC-FID to identify the fatty acid composition of the Canola oil. The analysis showed that the feed was mainly composed of C_{18-16} fatty acids. The Gas products were characterized by GC-TCD and revealed the presence of C_1 gases: CO, CO_2 and CH_4. No H_2 was detected in the gas products. The selectivity in the gas fraction was barely influenced by the composition of the HZSM-5 based samples and the results show a mean difference within ±1.0%.

A fractional conversion of close to 100% for all the tested Ni-loaded samples was observed, no fatty acids were detected in the OLP. Since the detected C_{18-16} fatty acids are liquids at room temperature, it was concluded that the amount of C_{18} fatty acids in the gas product was zero. When the HZSM-5 was loaded with Sn (atomic radius = 145pm), at higher loading %, (2.99 and 3.82%) of Sn, the conversion was lowered up to 77.9 and 91.4% from 100% that was observed for lower loading of 0.25 – 1.77%.

The organic liquid product fraction was characterized using GC-MS. An analysis was done for the thermo-catalytic products of six different groups of catalysts, namely: Ni-Aqueous promotion; Ni-AQ, Ni-Incipient Wetness promotion Ni-IW; Ni-Mechanical Mixing promotion; Ni-MM; Sn-Aqueous promotion; Sn-AQ, Sn-Incipient Wetness promotion; Sn-IW, and Sn-Mechanical Mixing promotion; Sn-MM. Each of these different metal loading/ promotions were done to understand how the products were affected by increasing the Metal Loading/ promotion. For each of the product streams, the metal loading/ promotion targets of 0.5%, 1%, 3%, 5% and 7% were used. Trends to relate the Metal loading/ promotion to the product output and fractional conversion were done for each metal for comparison of the different product streams. It was observed that for Ni-AQ, Ni-IW and Ni-MM the average amount of aromatics in the organic liquid product for the Metal loading/ promotion was 68.3%, 80.6% and 63.3% respectively.

From results it was observed that the activity of the Sn loaded samples increases in the production of various products groups such as Benzene, Toluene and Xylene (BTX) among other aromatics and, Ni activity was more towards Cyclopentane derivatives and Alkynes (XCA). The unpromoted commercial HZSM-5 catalyst produced 7.18% Xylenes, with no Cyclopentane Deravatives and Alkynes detected. Ni-loading exhibited increased catalytic activity towards XCA production for samples loaded using AQ and MM techniques. The samples loaded by IW technique showed activity towards producing Xylene but not Cyclopentane Derivatives or Alkynes. The introduction of Ni has increased the production of unsaturated hydrocarbons lighter than the C_{18} hydrocarbons such as: 1,5-Heptadien-3-yne, 1,3-Hexadien-5-yne, and 1-ethenyl-3-methylene-cyclopentene. The results obtained from this study show the selectivity toward BTX and other aromatics was lifted when HZSM-5 was promoted with Sn in comparison to the unpromoted HZSM-5 and Ni-HZSM-5. No Cyclopentane Derivatives and Alkynes were detected in any of the products of the Sn loaded samples.

Dedication

This study is dedicated to my parents, and all my 10 siblings who gave me the primary courage to study Chemical Engineering.

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CHAPTER 1

1.1 Introduction

Chemicals from fossil-based sources such as petroleum (crude oil), coal and natural gas form a very important part of the chemical industry that uplifts the well-being of the global population. However, this pronounced benefit to humankind through exploitation of fossils has also brought various problems to the globe, hence, stimulating research that explores the alternatives to the conventional source of chemicals. One of the greatest problems is that the continuous depletion of non-renewable fossils chemical sources is finite. Consumption without replacement will lead to an unsustainable source of the chemicals in the future (Shafiee and Topal 2009). At this junction, production of chemicals from renewable sources becomes vital. A number of technologies for the production of chemicals exist, i.e. pyrolysis, natural product extraction from plants, chemical synthesis using synthetic reagents amongst others. The main principle in the production of useful chemicals such as olefins, aromatics, paraffins and heavy hydrocarbons from fossil fuels is the carbon chemistry of fossils; crude oil contains many compounds with different carbons as a physical mixture. These compounds can be separated using fractional distillation to produce different products. The nature of carbon compounds allows a diverse spectrum of compounds to derive from crude oil, natural gas and coal through the carbon chain length transformation of these raw materials. Physical separation and chemical treatment technologies that make the manufacturing of chemicals also provides jobs for people, therefore it is important that a sustainable source of chemicals is established. Since crude oil can be purified using a physical separation method such as distillation, the different fractions that occur in different quantities have different demands on the market. Chemical engineers developed chemical treatment technologies such as catalytic reforming may to enhance a desired fraction by manipulating the carbon chain lengths (Turaga and Ramanathan 2003). These chemical transformation technologies presents an opportunity to extend the life span of the fossil resources.

Global warming is yet another problem caused by the burning and processing of fossil fuels to produce energy. The net carbon dioxide/ monoxide emitted to the atmosphere by fossil fuels increases the prevalence of these greenhouse gases, causing the greenhouse effect that eventually causes the increase in global temperatures (Hoel and Kverndokk 1996; Joshi, Dincer and Reddy 2010). While there are many other disadvantages of relying on fossil fuels for energy and chemicals, the use of fossil derived products and their harnessing technologies also cause acid rain, due to the emission of sulphur based pollutant compounds such as SO_2 in to the atmosphere (Omer 2008). Additionally, these pollutant materials ultimately reduce the quality of the air we breathe and could impose health problems.

Alternatively, to solve the problem of the non-renewable nature of fossils based feedstocks and their disadvantages to the environment, the chemical composition biomass derived feedstocks could provide a solution to the problem. Biomass materials are high in carbon. The carbon content of biomass and its derivatives can be physically and chemically transformed to different forms to suit energy and chemical needs to a considerable extent. Some authors, Jacobson and Delucchi, (2011); García-Olivares *et al.*, (2012); Breyer *et al.*, (2017) argued that a 100% renewable economy will provide lasting future solution. Furthermore, they stressed on biomass-derived oils (BDOs), being part of the promising renewable sources of energy and chemicals. BDOs were specifically identified to be a possible answer to the problems caused by the production of fuels and chemicals from fossils. Some of the focus points of the use of BDOs was based on the fact that their use would reduce the net CO_2 emissions into the atmosphere and substantially reduced the emissions of other pollutant chemicals such as sulphur compounds that occur as impurities in some crude oil reserves. BDOs in this work refers to oils produced directly from recently lived biomass (excluding algae and any other forms of aquatic life) using methods such as pyrolysis and extraction of oil from recently lived organisms. In order to use BDOs for the production of fuels and chemicals, such oils need to be upgraded to fuel grade chemicals and or converted to such chemicals that are of specified grades (Mukarakate *et al.,* 2014; Wu *et al.,* 2016). Upgrading is very important because the BDOs are usually viscous, have lower heating values; lower H:C ratios and high O:C ratios relative to conventional fuels (Mortensen *et al.,* 2011). Great effort to upgrade BDOs to a wide range of products was studied by other authors; however, this work focuses on the catalytic upgrading of vegetable oils, specifically canola oil, using HZSM-5 based zeolite catalysts to produce unsaturated hydrocarbons, and aromatics. There are two choices of catalytic procedures that are used to catalytically upgrade biomass-derived oils: high pressure catalytic treatment, such as hydro-treating and hydrogenation as reported by (Liu *et al.,* 2009; Lovás *et al.,* 2015) or low pressure catalytic treatment as reported by (Vichaphund *et al.,* 2014; Veses *et al.,* 2015; Engtrakul *et al.,* 2016). The high pressure methods target hydrogenated hydrocarbons by ensuring reducing environments usually achieved through the use of a reducing agent such as water or hydrogen. On the other hand, low pressure catalytic treatment occurs in reactors at atmospheric pressure and the oil being upgraded usually interacts with the catalyst at low pressure. This work applies low pressure catalytic treatment of canola oil over promoted HZSM-5 samples. The feedstock in this work is classified as a vegetable oil, as it is produced from seeds of canola plants by pressing, solvent extraction or through supercritical fluid extraction (Straccia *et al.,* 2012). This BDO therefore can be classified as renewable as canola plants can be planted and harvested within a short period of time.

In addition to CO_2 reduction based on the fact that plants convert atmospheric CO_2 to other forms of carbon in plants through photosynthesis, the source of vegetable oils and other BDOs suggest that the products of oil upgrading are not contaminated with pollutant sulphur compounds. This is based on the background that the composition of biomass has little to relatively no pollutants chemicals such as sulphur. In this work, promoted HZSM-5 catalysts were used to upgrade canola oil based on the advantages of these materials as reported in the fore-reported literature.

To upgrade the canola oil, the target products should be identified to assist in making a better choice for a catalyst. For example, HZSM-5 has shape selectivity, that spearheads the restructuring of light hydrocarbons and reshaping of long and heavy molecules to cut-off sizes due it’s zeolite pore size (Chen and Garwood 1986; Adjaye, Katikaneni and Bakhshi 1996; Creyghton and Downing 1998; Jae *et al.,* 2011). Another advantage of HZSM-5 is the heterogeneous acidity that allow cracking, oligomerisation, isomer formation and aromatization (Huang *et al.,* 2009; Engtrakul *et al.,* 2016). These catalytic properties of HZSM-5 pose a viable option for the upgrading of canola oil to lighter hydrocarbons in the gasoline range.

In addition to these favourable reactions, solid catalysts such as HZSM-5 form a heterogeneous mixture with the liquid and gas products, making it easier to separate with the product after the reaction is complete. These advantages associated with

HZSM-5, allowed this catalyst to be applied in the conversion of both vegetable and wood-derived oils to useful chemicals such as benzene, toluene and xylenes (BTX) and transportation fuel (Chantal *et al.,* 1984). Furthermore, in other studies, HZSM-5 was proven to selectively convert oxygenates to gasoline range hydrocarbons (Thring, Katikaneni and Bakhshi 2000; Rownaghi and Hedlund 2011). Generally, it is necessary that the products that emanate from the conversion process meet certain requirements. This makes robust and highly selective catalysts very useful in the prospects and production of specialized chemicals.

Looking at canola oil as a vegetable oil, it is notable that unlike wood pyrolysis oil, vegetable oils can be converted to fuel range chemical even at lower fractional conversion rates. This conclusion is drawn from the fact that vegetable oils were reported to run diesel engines. This suggests that vegetable oils have fuel properties and are a potential renewable oil source to support the transportation fuel sector. The use of vegetable oils in the transportation industry is however not new. For example, peanut oil was used as a fuel in diesel engines in 1900, but this option was not commercialised since it was much cheaper to run engines on fossil fuel derived hydrocarbons as reported by Olusola *et al.,* (2010). Unfortunately, other authors also reported the same idea; that the economic viability of using of vegetable triglycerides as fuels as did not have sufficient support (Srivastava and Prasad 2000; Drenth *et al.,* 2014). At this junction, it gives us the need to investigate modern agricultural methods to harness massive industrial quantities of these oils, collect waste and used oils to economically mitigate the problems associated with the economic return in the use of vegetable oils as fuels or chemical sources. Other than economic reasons, the efficiency and chemical stability of vegetable oils were not favourable to commercialize them as fuels (Drenth *et al.,* 2014). Going back to upgading oils, the approach should then include the efficiency and stability of the chemical products of the upgrading process. It is also important to study chemical transformation of these materials using a much more economic technology of manufacturing useful chemicals from vegetable oils that may not be necessarily fuels. That being said, it is not only the cost that plays a role in the technology of the manufacturing process. Sustainability, thus, continuous supply and regeneration of the source product and raw materials are also of great importance. The globe cannot continue to rely only on fossils for the production of fuels and useful chemicals such as olefins since these are non-renewable sources. The development of renewable alternatives is urgent, especially in the quest to securing a sustainable economy for the future.

1.2 Biomass as a source of chemicals

Many materials contain carbon. For example, natural rubbers, algae, and plant materials. To draw a line and outline the more specific boundaries, this work considers biomass as matter that exists as a non-fossil, complex of recently lived organisms' organic–inorganic solid material made by natural and human activity routes, that include: (a) components created after cultivation of land and any other water generated flora through photosynthesis, and or produced by animal or human digestion; and (b) products, by-products and or waste derived from the processing of the above natural materials.

Over the past years, the search for feedstocks to produce chemicals has been very intense. To achieve this, scientists and engineers studied the processes of converting biomass to some of the chemicals that are of high demand, especially fuel chemicals. For example, biomass gasification has been used to produce hydrogen, methane and syngas through biochemical pathways (Sikarwar *et al.,* 2016). Thermochemical conversion of biomass to syngas is also one of the gasification methods used as an intermediate step to produce the raw materials of chemical synthesis i.e. syngas that is further converted to many other chemicals through the production of light olefins (Aasberg-Petersen *et al.,* 2001). A further discussion of the applications of light olefins is outlined in section 2.2.1 of this work.

Biodiesel production from biomass is another production of fuel from biomass technology that uses lipids or fatty acids to react with alcohols to produce alkylesters (Gunawan *et al.,* 2014). Since biomass has demonstrated great potential in the production of chemicals, it is important to study the chemical setup of biomass to better elucidate possible reactions that govern conversion. These materials are mainly composed of carbon based structures such as: cellulose and hemicellulose, sugars, lignin, natural plant nutrients including but not limited to amino acids, proteins and vitamins, oxygenates such as ethers, carboxylic materials such as fats, resins, oils, and waxes (Vassilev *et al.,* 2010). The technologies used in the fuel harvesting from biomass target the carbon structures in the biomass as the energy source. Even biodiesel is governed by the combustion of carbon contained in the alkylesters. Other than fuel, chemicals such as pharmaceuticals, essential oils and cosmetics just to mention a few, also derive from biomass.

Woody biomass also finds application in the production of fire wood that is used for cooking and heating, especially in rural communities. Industrially, the woody biomass that usually contains higher content of carbon is also burned for charcoal and production of activated carbon. This extents the use of woody biomas to the water treatment industry where activated carbon is used (Mante *et al.,* 2014). Recently, the upgrading of biomass to more specialized products in the petrochemical industry has been on going. To achieve this, highly selective catalysts are used. It is therefore necessary to examine the physicochemical properties of the feedstocks to better understand the technical approach of catalytic treatment of biomass based feedstocks.

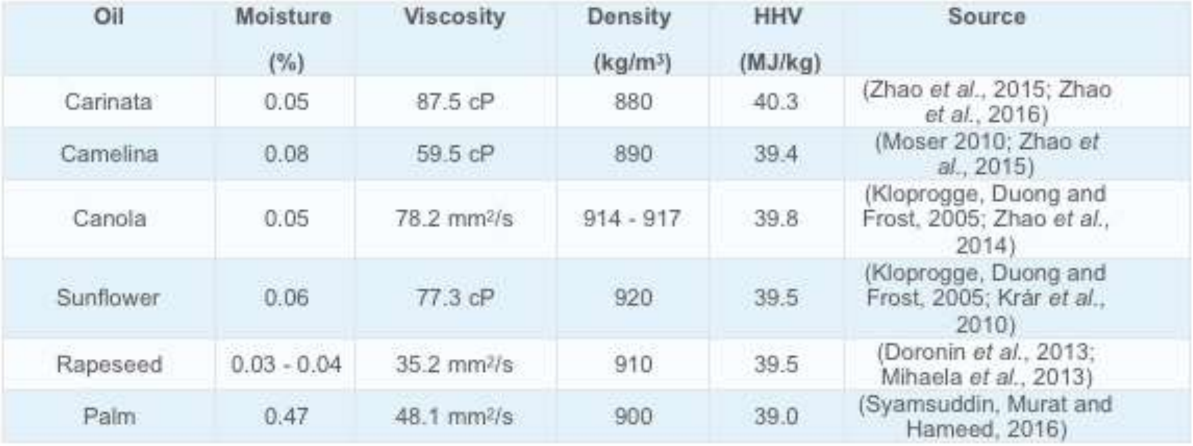
1.3 Physicochemical properties of pyrolysis oils and vegetable oils

The physicochemical properties of BDO depend on the part of the plant from wich they derive. To better categorize different oils, it is important than they are classified either as vegetable oils or pyrolysis oil. This classification provides an idea on the possible properties; physical and chemical, of such an oil. This is due to the fact that vegetable and pyrolysis oils derive from distinctly different parts of recently lived plants as mentioned in section 1.1. The concentration of carbon and its forms will differ in different parts of the plants. To outline the variance of the of carbon forms and content

Table 1 summarizes the typical physical properties of selected vegetable oils and their higher heating value (HHV). *Table 2* displays the (C, H, O, N, S) elemental analysis of some common vegetable oils. Then,

Table 3 reports the chemical components of pyrolysis oils to compare and contrast both vegetable and pyrolysis oils in terms of composition. Lastly, *Table 4* further compares the general properties of pyrolysis oils to crude oil as the aim is to evaluate how the BDOs relate to petroleum.

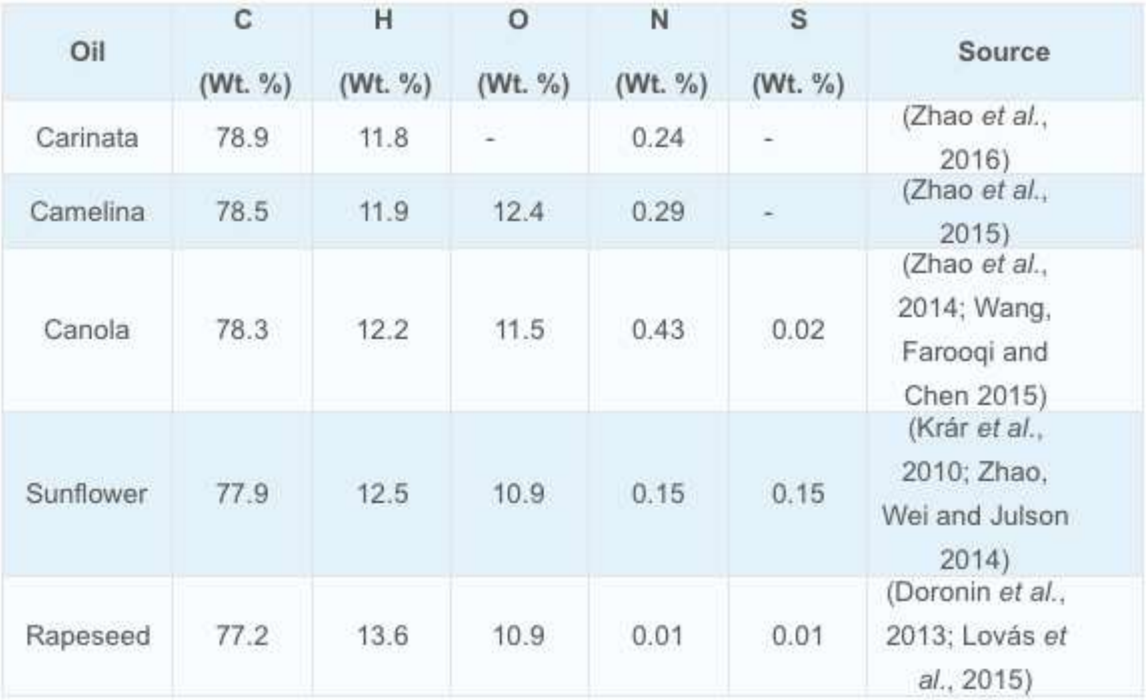
Table 1. Typical properties of selected vegetable seed oils.



Oil	Moisture (%)	Viscosity	Density (kg/m^3)	HHV (MJ/kg)	Source
Carinata	0.05	87.5 cP	880	40.3	(Zhao *et al.*, 2015; Zhao *et al.*, 2016)
Camelina	0.08	59.5 cP	890	39.4	(Moser 2010; Zhao *et al.*, 2015)
Canola	0.05	78.2 mm^2/s	914 - 917	39.8	(Kloprogge, Duong and Frost, 2005; Zhao *et al.*, 2014)
Sunflower	0.06	77.3 cP	920	39.5	(Kloprogge, Duong and Frost, 2005; Krár *et al.*, 2010)
Rapeseed	0.03 - 0.04	35.2 mm^2/s	910	39.5	(Doronin *et al.*, 2013; Mihaela *et al.*, 2013)
Palm	0.47	48.1 mm^2/s	900	39.0	(Syamsuddin, Murat and Hameed, 2016)

The elemental analysis of vegetable oils compared to pyrolysis oil displays many elements in common, C, H, O and other minor S and N. The amount of sulphur and nitrogen in both cases is low, which is favoured in fuel compositions as this are pollutant sources and pronounced amounts would lower the heating values of fuels derivatives. The carbon content of vegetable oils reported ranges from 69 - 78.9 wt. %. Hydrogen from 10.8 – 13.6 wt. %. A higher molar ratio of H : C represents more saturated hydrocarbons. The H:C ratio for vegetable oils is therefore higher than that of pyrolysis oil who's carbon and hydrogen contents are 55 – 65 wt.% and 5 – 7 wt.% respectively (Al-Sabawi, Chen and Ng 2012).

Table 2. Elemental composition of selected vegetable oils.



Oil	C (Wt. %)	H (Wt. %)	O (Wt. %)	N (Wt. %)	S (Wt. %)	Source
Carinata	78.9	11.8	-	0.24	-	(Zhao *et al.*, 2016)
Camelina	78.5	11.9	12.4	0.29	-	(Zhao *et al.*, 2015)
Canola	78.3	12.2	11.5	0.43	0.02	(Zhao *et al.*, 2014; Wang, Farooqi and Chen 2015)
Sunflower	77.9	12.5	10.9	0.15	0.15	(Krár *et al.*, 2010; Zhao, Wei and Julson 2014)
Rapeseed	77.2	13.6	10.9	0.01	0.01	(Doronin *et al.*, 2013; Lovás *et al.*, 2015)

The high oxygen content of pyrolysis bio-oil can be justified by the chemical components present in the oil mixture. As shown Oxygenated compounds dominate the composition of pyrolysis oils, contributing to the high oxygen of the oils (Gayubo *et al.,* 2010).

Table 3. Chemical components of pine sawdust pyrolysis bio-oil (Gayubo et al., 2010).

Component group	wt. %
Organic acids	26.17
Ketones	27.03
Aldehydes	19.33
Ethers	0.94
Phenols	8.20
Alcohols	11.45
Levoglucosan	3.94

Both crude and bio-oils are organic matter derived. Except for bio-oils being generated from recently lived organisms, the energy basis of both oils is stored in their carbon-hydrogen content that is derived from decayed organic matter. Pyrolysis oil is a complex mixture of different molecules that originate from the pyrolysis of lignin, cellulose and hemicellulose (Liu *et al.,* 2008). The chemical composition of the crude oil is usually a function of the source, i.e. it varies from one reserve to another. *Table 4* below, reports typical values as reported in literature. The definite values a reported on the average basis.

Table 4. Physical properties and elemental composition of the pyrolysis bio-oil and crude oil (Mortensen et al., 2011; Al-Sabawi, Chen and Ng 2012)

Physical Property	**Bio-oil**	**Crude oil**
Moisture %	15 – 30	0.1
pH	2.8 - 3.8	-
Density (kg/l)	1.05 - 1.25	0.9
Viscosity (cP, at 50°C)	40 - 100	180
HHV (MJ/kg)	16 – 19	44
ELEMENTAL (%)	**BIO-OIL**	**CRUDE OIL**
C	55 – 65	83 – 86
H	5 - 7.0	11 - 14.0
O	28 – 40	<1
S	<0.05	<4
N	<0.4	<1
Ash	<0.2	0.1

From the data reported it can be concluded that pyrolysis oil contains more moisture than typical vegetable oil. Additionally, the vegetable oils contain long chains fatty acids (fatty acids are insoluble in water) that influence their viscosity, melting and boiling points (Stavarache *et al.,* 2005). Another evidence of fatty acids in vegetable oils, saturated and unsaturated is the reported composition of biodiesel produced from edible and non-edible vegetable oil (Sajjadi, Raman and Arandiyan 2016). Pyrolysis oils on the other hand contain: aldehydes, ketones, and alcohols that are miscible with water, especially at low molecular weights, therefore enhancing ability to absorb moisture. Vegetable oils have a higher heating value (HHV) than that of pyrolysis oils, in agreement to their lower ash content, chemical complexity i.e. the prevalence of carbon rich triglycerides (Srivastava and Prasad 2000). Additionally, vegetable oils are usually refined and have lower oxygen content than pyrolysis oils. The viscosity of pyrolysis oil is higher, reaching up to 100 cP (Al-Sabawi, Chen and Ng 2012).

1.4 Statement of the problem

Generally, across the globe, governments and economies invest resources and time in terms of conservation of resources such as chemicals, fuels and water. Ultimately, employment of good practices to save these limited resources has become a norm due to population growth and increased scarcity. Additionally, environmental health and safety is also much considered by many users of chemicals and fuels, and this has led to concerns on pollution and emission footprints.

Currently, a great portion of chemicals, especially hydrocarbons, solvents, fuels and polymers that support the chemical industry, are produced from fossil fuels. Due to their non-renewable nature, it is necessary that the conservative measures are put in place to save these valuables. Nonetheless, conservation alone cannot be sufficient, since industrial and domestic demands for these chemicals impart a lot of pressure on the fossil fuels.

At this junction, the need for development and optimization of green technologies, especially production of these chemicals from renewable sources such as biomass and its derivatives becomes an important engine to ensuring a reduced pollutants environment, sustainable sources of chemicals and fuels, and economic emancipation through creation of jobs and business opportunities in the biochemical-biofuel industries.

Research has shown that the vegetable oils and biomass can be converted to a wide range of petroleum product equivalents (Lovás *et al.,* 2015; Bayat and Sadrameli 2017). Currently, 10 - 20 million hectares of land in South Africa is covered with encroachment bush, and around 10 million hectares with invasive alien plants (Stafford *et al.,* 2017). It possible to rehabilitate such land masses for oil seed production while harvesting the current vegetation for biomass pyrolysis. The problem of bush encroachment is not only a South African problem, for example, the neighbouring Namibia has an estimated 26 – 30 million hectares of bush encroachment that is estimated at about 54 million tonnes that could be harvested at 2.7 million tonnes per year (Stafford *et al.,* 2017).

The current problem to solve is to collect scientific and technology data that suggests how this amount of biomass may be used to generate revenue that can be used to commission master projects in the production of biomass derived oils that may ultimately be converted to petrochemicals of high value. Additionally, waste vegetable oils from food outlets makes a good raw material for conversion to fuel while reducing water treatment costs (Kulkarni and Dalai 2006; Talebian-Kiakalaieh, Amin and Mazaheri 2013). Specific to this work, research questions such as whether canola oil can be converted to useful and value added petrochemical over promoted HZSM-5 based catalyst will be answered. The data generated may be used to aid process and industrial related projects to carryout techno-economic analyses to validate the viability of this method of producing useful chemicals from crude canola oil.

Furthermore, the study yields more evidence on the use of transition metals as catalytic promoters and can be used as selectivity enhancers in chemical processes for the production of high value chemicals.

1.5 Aims and objectives

The aim of this work was mainly to promote HZSM-5 catalysts for the application in the conversion of BDOs to a wide spectrum of hydrocarbons.

The study paid a closer look at the following specific objectives:

a) To determine the effect of metal loading on the catalytic conversion of canola oil to hydrocarbons and fuel range chemicals.
b) To determine the effect of metal loading on product distribution during the catalytic conversion of canola oil to hydrocarbons.
c) To carry out a comparative study between Sn and Ni-HZSM-5 catalyst in canola oil catalytic conversion.
d) To establish the relationship between promotion techniques and catalytic activity.

1.6 Scope of the specific objectives

Metal loading was used to modify the physical and chemical properties of the unpromoted catalysts (HZSM-5). Two metals; Nickel and Tin, were loaded on the unpromoted HZSM catalyst in different concentrations (refer to *Table 5*). The loading was achieved using different techniques but the same amount of metal source was used for each set of samples

- The effect of metal loading on the catalytic conversion was studied by quantifying the fraction of feed reacted while varying the amount of metal loaded on the unpromoted catalyst.
- To determine the effect of metal loading on the product distribution, the chemical identity, and selectivity/ product distribution of the product stream was reported and an analysis was performed as the amount of metal loaded was varied by comparing the products of HZSM-5 and those of the loaded samples.
- To compare Sn-HZSM-5 and Ni-HZSM-5, a detailed analyses of the products produced by both Sn and Ni loaded catalysts was performed, compared and contrasted with respect to the quality and quantity of products.
- To establish the relationship between promotion techniques and catalytic activity, samples with the same loading percentage from different techniques

were compared to establish activity of catalysts using product yield, and product distribution.

CHAPTER 2

2.1 Liquid Fuels and the Chemical Industry

Petrol and diesel are the main liquid fuels for the automobiles. With the continuous extraction of fossil fuels from the earth and increase in the demand for energy imposed by population growth and industrialization, it has become evident that the demand for fossil fuels will rise unless alternative energy sources are established (Yıldız 2018). Unfortunately, not all regions of the world have access to the fossil reserves. Luckily, the distribution of renewable resources such as biomass are more pronounced than that of fossil fuels across the world. The unequal distribution of fossil fuels across the world poses economic threats to nations that do not have such reserves as the scarcity and demand becomes pronounced. Development and industrialization of many nations came at the cost of natural resources, mainly non-renewable energy sources coal, petroleum, and natural gas (Hoel and Kverndokk 1996).

Besides the pronounced growth and development through industrialization of the nations, these fossil fuels also pollute the atmosphere with GHGs and pollutant emissions causing global warming. Forecasts estimate that the world energy demands will increase by more than a third over the next 2 decades and demand for petroleum is much likely to increase by 30% to about 111 million barrels per day by the year 2035 as reported by the US Energy Information Agency, (EIA 2017). This noticeable demand for energy resources increases the risk of pollution and global warming as depletion of fossil fuels continues. The demand has accelerated a big eye on research and development of technologies for renewable energy. On the other hand, the chemical industry relies heavily on the fossil fuels, especially in the production of polymers, solvents and plastics amongst others from aromatic compounds and olefins. The increased demand might also have an impact on the competition between fuel and other consumer products.

The EIA further reported that the transportation business is the largest and currently the fastest growing energy industry in the world. More than 33% total energy consumed globally is linked to transportation with over 95% of this sector’s energy produced from fossil fuels. This fast growing industry consumes a great amount of petrochemical feedstocks that mainly derive from the “hot cake’’ commodity, crude oil through naphtha reforming and steam cracking of condensates and alkanes to maximise transportation fuel production as shown in *Figure 1*. Aromatic compounds that are building blocks of some consumer products are also used in gasoline motor vehicle fuel as additives (Demirbas *et al.,* 2015). Now that there are high fuel production volumes, it possess a threat that the demand for aromatics with rise directly with transportation fuel. In other words, as the transport sector continues to grow, the production of gasoline and diesel are likely to consume a lot of the crude oil through catalytic reforming to meet the demands, compromising the balance in other chemical commodities. Consequently, even though exploration and discovery of oil reserves continues, the chemical industry is likely to suffer due to pronounced growth.

The search for alternative sources is on, especially concentrating on the renewable sources where biomass is one of the focus points. BDOs can be produced and be made readily available renewable oils that can supplement crude oil which is currently the main source of hydrocarbons (Al-Sabawi, Chen and Ng 2012). BDOs are also environmentally friendly, so, lately there has been a great vision on production of clean fuel range hydrocarbons from biomass, especially from wood, in prospects to reduce carbon emissions and other pollution forms caused by the use of crude oil (Demirbas 2009). These BDOs are produced by thermochemical conversions through pyrolysis and high-pressure liquefaction of biomass, or by biological conversion, fermentation, and aerobic digestion (Veses *et al.,* 2015) and oil seed pressing (Zhao *et al.,* 2014). Pyrolysis oil, vegetable and plant oils are regarded BDOs because they derive from recently lived organic materials. These methods produce oils with high water and oxygen content, low heating value, with an exception of triglyceride based vegetable oils (Sajjadi, Raman and Arandiyan 2016), and high acidity, making it unfriendly to exploit them as fuels (Veses *et al.,* 2015).

To solve this problem, upgrading BDOs using ZSM-5 zeolite based catalysts is essential. In order to develop knowledge of the reactions that occur during zeolite catalytic upgrading of BDOs, (Horne and Williams 1996), studied the catalytic reactions of furfural, methanol, and cyclopentanone over ZSM-5 catalyst. In their study, they established that ZSM-5 led to the formation of water, oil, gas and coke. In addition to oil and gas production from oxygenated compounds, ZSM-5 has proven to be an efficient catalyst in upgrading BDOs when applied as an additive to Y-zeolite catalysts, reducing coke and char in the upgraded oil (Mante *et al.,* 2014). The protonated form of ZSM-5 possess further enhanced its catalytic properties for upgrading BDOs and it increased the calorific value in the upgraded oil in addition to dewatering (Vitolo *et al.,* 1999). The results in this study overlap with the production of organic chemicals from BDOs because the reactants studied were closely related to the composition of BDOs, especially common wood pyrolysis oil. BDOs were also successful aromatized over HZSM-5 based catalysts (Tshabalala and Scurrell 2015; Lorenzetti *et al.*, 2016). The significance H-ZSM-5 is that it is another achievable form of ZSM-5 which is more acidic compared to unprotonated form, ZSM-5, and was found to be remain chemically and thermally stable after protonation (Vitolo *et al.,* 2001). The acidity of the catalyst improves its efficiency in converting the oxygenated compounds to fuel range chemicals. It is this acidity that increases the calorific values of the upgraded BDOs through the efficient deoxygenation (Vitolo *et al.,* 2001; Mante *et al.,* 2014). The thermo-catalytic conversion of BDOs ZSM-5 zeolites to fuel range chemicals is a potential solution to the bio-fuel market. Biomass-based hydrocarbon fuels have energy density similar to crude oil fuels in comparison to biodiesel (Wu *et al.,* 2010). This makes biomass a renewable hydrocarbon fuel source that could help to meet the increased standards of fuel economy imposed by governments to the automobile sector. The potential for biomass to chemicals (BTC) has been demonstrated and this is well researched. It could also be viewed as a promising rescue to the strains imposed on the chemical industry by the rapid expansion of the transportation sector. One of the strong point in BTC is that renewable energy sources reduce greenhouse gas (GHG) emissions and do not constitute a net contributor to environmental pollutants, making them environmentally friendly fuels.

Biomass, being one of the most readily available renewable sources of energy, and considered to be chemically possible to convert to biofuels by two broad categories of processes i.e. biological and thermochemical conversion methods gives a stepping stone into the future of alternative sources of chemicals (Al-Sabawi, Chen and Ng 2012; Yigezu and Muthukumar 2014)**.** Additionally Biofuels reduce costs and are compatible with the current transportation infrastructure (Zhao *et al.,* 2015). Pyrolysis of lignocellulosic biomass and extraction of vegetable seed oils can be used to produce refined vegetable oils, carbon rich pyrolysis oil and gaseous alkanes. It is worth noting that vegetable oils that are not converted to biofuel cannot be used efficiently to fuel machines and engines directly, unless they are upgraded. These oils on the other hand are also viscous and their acidity for use directly as biofuels is high (Wang *et al.,* 2016). In the energy industry, vegetable oil is primarily upgraded to biodiesel, by catalytic trans esterification (Sankaranarayanan *et al.,* 2013; Gunawan *et al.,* 2014). The current dynamics of the energy industry and crisis calls for chemical products beyond just biodiesel (Choudhary and Phillips 2011). Upgrading oils to fuel range chemicals mainly involves converting components through: cracking, alkylation, aromatization, isomerization and oligomerization of hydrocarbons (Creyghton and Downing 1998; Degnan 2003; Bellussi and Pollesel 2005). Upgrading vegetable oil for use as a fuel provides both environmental and economic solutions to the energy industry with reference to global distribution and renewability (Kloprogge, Duong and Frost 2005).

The success of upgrading of vegetable oils to usable fuel is not a coincidence as such, the oils are composed of triglycerides and molecules with carbon chains related to the liquid fuels derived from fossil fuels (Domínguez-Barroso *et al.,* 2016). These triglycerides are also enhancers of the oxygen content of the oil together with esters carboxylic acids and other oxygenated organics. The composition therefore requires de-oxygenation and hydrogenation processes to be part of the upgrading in order to synthesize high energy density chemicals or hydrocarbon molecules. There are several technologies used for the conversion of vegetable to biofuels. With each technology involving chemical and physical transformation, different technologies have their own advantages and disadvantages. Trans-esterification, pyrolysis, hydro processing, fermentation and catalytic cracking are some of the current methods used to convert vegetable oils to biofuels. This study, however, will focus on catalytic upgrading of vegetable oils, reviewing the role of ZSM-5-based catalytic cracking. Catalytic cracking may be used to achieve a chemical conversion at a relatively low energy input to produce hydrocarbons (Ahmad *et al.,* 2016). With higher product yield and lower energy requirement, catalytic cracking of vegetable oil could be a cost effective technology to produce hydrocarbons for biofuels. This is a promising solution to clean energy for the environment. The application of bio-hydrocarbons as fuel in engines for automobiles may require few modifications to the current engines while promising reduction in GHG emission.

2.2 Petrochemical industry

The main aim of the petrochemical industry is to produce consumer products from petroleum and other petrochemicals. Some of the important petrochemicals and derivatives include olefins, aromatics in addition to the consumer chemicals: polymers, feedstocks and blending components (Chohan *et al.,* 2018). The chemical complexes used to produce these petrochemicals are consumed. Unfortunately, chemical such as aromatics occur in relatively small concentrations in crude oil. Another important group of chemicals produced by catalytic reforming of crude oil fractions is the olefins. Olefins are the building blocks of the polymers and oligomers that are used in the manufacturing of plastics, fibres, lubricants and gels amongst other consumer product (Amghizar *et al.,* 2017). Aromatics are used as feedstocks for other petrochemicals that have aromatic rings in their structure such as dyes, synthetic detergents, polyurethane, fibres, plastics and also in the pharmaceutical drugs such as acetylsalicylic acid (asprin) using an aromatic derivative, salicylic acid and acetyl anhydride. *Figure 1* shows a general algorithm of the conventional source of production of consumer products.

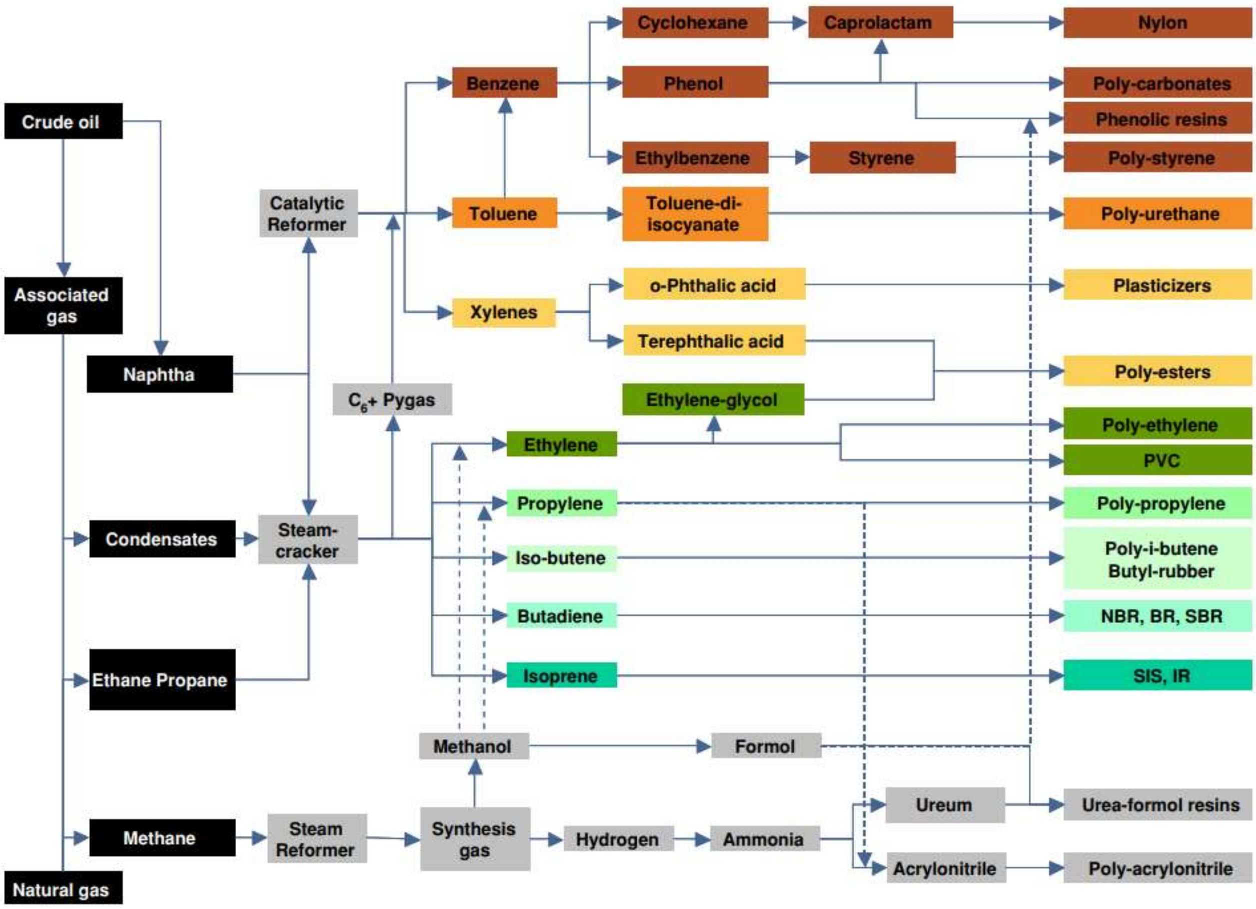


Figure 1, Production of petrochemicals from crude oil and natural gas (Vermeiren and Gilson 2009).

Natural gas and crude oil are the major sources of most of the synthetic materials that we use on a daily basis. It is inevitable that the population growth will exert a lot more pressure on these natural resources. The materials such as plastics, polymers and others will continue to be in great demand to support the population. There is no doubt, it is urgent that renewable sources of chemicals listed in *Figure 1* be explored. In this work, the production of such chemicals will be demonstrated. The categories of useful chemicals were identified as: BTEX, cyclohydrocarbons, phenols and their derivatives, organic acids and heavy hydrocarbons such as polymers and plastics.

2.2.1 Olefins

Olefins are some essential chemical compounds to the petrochemical industry. They one of the most valuable group of chemicals due to their chemical properties that allow them to be converted to other chemicals of synthetic choice (Rahimi and Karimzadeh 2011; Huang *et al.,* 2012; Botas *et al.,* 2014). Olefins are unsaturated hydrocarbons that contain at least a set of double and or triple bonds in their structure. The multiple bond chemistry is what allows olefins to be reactive and make them good synthesis raw materials. Quann *et al.*, (1988), reported the use of olefins in oligomerisation reactions. Furthermore, Alderson, Jenner and Lindsey, (1965), also reported the use of olefins in addition reactions for producing other chemicals such as substituted organic chains. Oligomerisation of light olefins especially ethylene to produce higher was commercialised in 1968, developed by the Shell Development Company's laboratories in Emeryville, California (Olivier-Bourbigou, Chodorge and Travers 1999). This marks the basis of the confidence that the production of both light and heavy olefins will continue to be of great contribution to the petrochemical industry, especially through exploiting sustainable renewable feedstocks such as pyrolysis and vegetable oils. Ethylene, propylene, and butylene are important feedstocks for polymer production (Jiao *et al.,* 2016; Zhong *et al.,* 2016).

Conventionally, the production of olefin depend extensively on the production of natural gas and crude oil fractions. This is due to the fact that light olefins are derived from syngas and steam cracking of hydrocarbons at elevated temperature. The hydrocarbons are produced from fossils. Syngas is converted to methanol as feedstock for methanol-to-olefins (MTO) process. The source of methane for syngas, and the petroleum fractions providing hydrocarbons have been the source of olefins for a long period of time in the history of petrochemicals. The process has been widely optimized to save materials and reduce costs over the years to build an economically viable process for the manufacturing of important consumer products made from olefins. The sad reality is that the demand escalates for these consumer products even though the main production method has been based on fossils resources that have an undesirable net carbon emission on the environment. Additionally, it is very difficult to adopt new methods if their economic viabilities are not well revised and developed. Production of olefins from shale gas project an opportunity in diversity of feedstocks. Even though shale gas is non-renewable, cracking of shale gas opens up opportunities for C_3/C_4 olefin production (Bruijnincx and Weckhuysen 2013). Another pathway for the production of olefins is the coal-to-olefins (CTO) technology that is aided by the gasification of coal (Xiang *et al.,* 2014).

2.2.2 Aromatics

Aromatic compounds especially the famous benzene, toluene, xylene, ethyl benzene (BTEX) are widely used as raw materials for reactions which are applied in the production of synthetic materials such as synthetic organics; substituted benzenes are the major consumer of benzene due to the versatility of benzene through: alkylation, acetylation, halogenation and other reaction pathways. The BTEX are also blending up to 30% of gasoline other than making consumer good (Mendoza-Domínguez A, Romero and Caballero-Mata P 2010). Toluene is used as an organic solvent and a raw material for benzene derivatives such as benzoic acid and other chemical building blocks. Conventionally, BTX were produced through coal tar distillation that results from carbonization. The evolution of the industry has added the introduction of steam cracking, catalytic reforming of low octane naphtha, and dehydrogenation of naphthalene, isomerization of alkanes and naphthene, and dehydrogenation of cycloalkanes (Vermeiren and Gilson 2009).

2.3 Production of useful chemicals and catalysis

Transition metal catalysts and synthetic zeolites have played an important role in the petroleum industry as catalyst. Thanks to the Brønsted acidity, porosity and crystallinity of zeolites, the chemical transformations such as cracking are possible. The versatility of these material has allowed for the manipulation of physical and chemical properties to make them highly robust and selective (Singh and Ekhe 2015). Generally, nature does not present commodities in the form that are refined and usable to man. This is not an exception to the composition of crude oil. For example, most of the crude oils do not have a substantial amount of olefins and aromatics compared to other components. Since the demand of these chemicals increases due to their chemical applications, it is necessary to maximize their production. Chemical treatment of naphtha; reforming, is one of the methods used to convert the hydrocarbons in naphtha to aromatics and alkanes that may be dehydrogenated for olefin production amongst other products such as liquefied petroleum gas (LPG) and hydrogen gas as by-products (Ali *et al.,* 2003; Shakoor 2011). The influence of catalysts becomes very important in catalytic reforming, to ensure that products meet specified requirements.

Another chemical transformation technology used in the production of petrochemicals is the Fischer-Tropsch Synthesis (FTS). This technology uses syngas as the raw material for the production of petrochemicals. The catalytic conversion of syngas to linear paraffins, primary alkenes and some oxygenates (Dry 1999). Transition metal based catalysts have traditionally been known for the Fischer-Tropsch reactions, with Nickel (Ni) and Cobalt (Co) based organometallic compounds reported to produce higher molecular weight hydrocarbons and other organic (Schulz 1999). The FTS is regarded as an alternative means of production in the petrochemical industry. Even though the processes is not using renewable feedstocks commercially, it is compatible with possible future renewable sources of syngas. Additionally, it is a great milestone for nations that do not have reserves of petroleum. South Africa and Malaysia have benefited from the FTS technology in cutting external imports of petrochemical (Amghizar *et al.,* 2017). MTO also uses syngas to produce olefins. The olefins from the MTO process are then ready for being converted to a wide range of petrochemicals over suitable catalysts (Stöcker 1999). The MTO process is a bridge to the methanol to the methanol-to-hydrocarbons (MTHC) technology. The production of MTHC can be summarised by recognising the main chemical reactions as shown below:

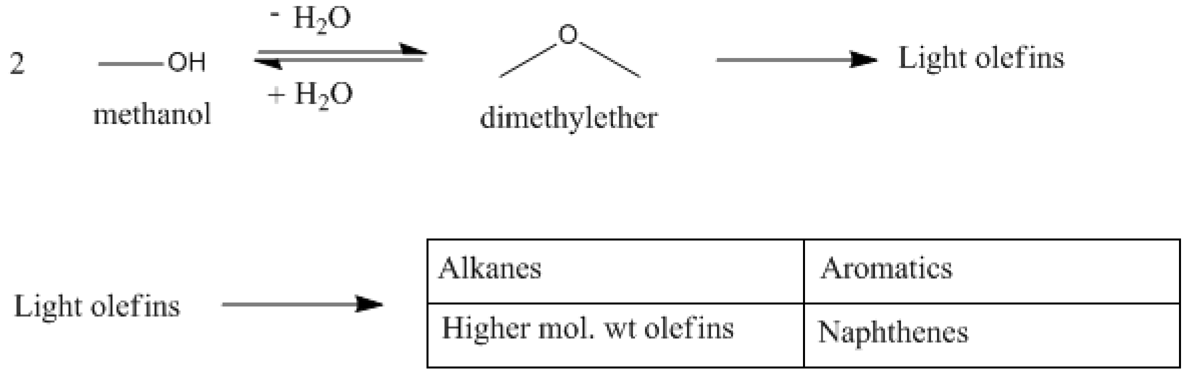


Figure 2, Reactions for the methanol to hydrocarbons technologies

Figure 2, expands the idea that light olefins are the building blocks of the petrochemical synthesis. Production of light olefins from renewable feedstocks such as Canola oil could pose sustainable supply of materials to the petrochemical industry in the future. Some of the technologies used in these chemical manufacturing include the Friedel-Crafts reactions and Zeolite catalysed synthesis.

2.4 Zeolite catalysts in petrochemical production

Zeolite materials dates back more 1756 since their discovery as minerals that gave up a lot of water upon heating them. This led to the name zeolite, derived from Greek ζέω, read as zéo, that means to boil and λίθος, read as líthos which means stone (Cundy and Cox 2003). The natural zeolites that were then known have not been used much, except being kept in the collections of minerals. Eventually, the studies conducted later led to the realization that zeolite materials find good applications in the areas of: adsorption, ion exchange and catalysis (MacHado *et al.,* 2005). In this work, the application of zeolites as catalysts is considered. As catalysts, zeolites are identified to be highly shape selective. The shape selectivity is mainly associated with molecular sieving ability of the zeolites (Degnan 2003; Jae *et al.,* 2011). The ability of zeolites to be shape selective and robust catalysts has also driven the advances in development of synthetic zeolite catalysts. In the petrochemical industry, the zeolites have developed to be probably the most important catalyst in the industry. Great effort has been invested to make zeolites industrial catalyst today. The first synthetic zeolites were the zeolites X,Y and A (Xu *et al.,* 2010). The zeolites are classified by their structure at microscopic level. While many other zeolites are also very active, this work applies the ZSM-5 type catalysts. The ZSM-5 materials have a unique structure and morphology that is classified as Mobil Five (MFI) that may assume nanorod orientation, fibre-sized amongst other characteristic features. *Figure 3* shows the porous characteristics of the sheets and the channel structure of ZSM-5.

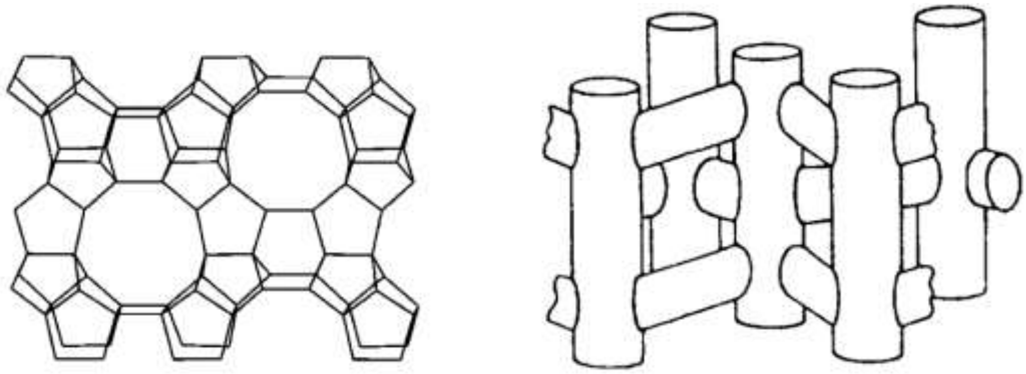


Figure 3, Porous voids and rod-like and channel structure of ZSM-5 (Xu et al., 2010).

ZSM-5 has competed vividly in the application as a catalyst that was used in cracking and production of light olefins and production of gasoline range products in fluid catalytic cracking (FCC) the early oil cracking process (Enos 1963). Discovered in 1965, ZSM-5 only found commercial applications in 1983 (Degnan, Chitnis and Schipper 2000). By then, the zeolite Y was used commercially and was continuously improved (Lutz 2014). From figure 3, the porosity of the material and then channels in the structure of ZSM-5 illustrates the physical property of the material's ability to work as a molecular sieve. The beginning of the trials to commercialise the ZSM-5 in the FCC did not portray its competitiveness. The final experiments showed how ZSM-5 could upgrade heavier fractions of the FCC to high octane number of gasoline (Degnan, Chitnis and Schipper 2000). The other catalytic process in the refineries is the hydro-cracking (HDC). The FCC is applied to produce the gasoline fuels, the HDC produces diesel fuel and little amounts of kerosene. Base oil is also produce when the HDC products are hydrogenated (Öhlmann 1999).

2.4.1 Why ZSM-5 catalysts?

There are over 170 zeolites register by the International Zeolite Association (IZA) (Vermeiren and Gilson 2009). The Mobil Company has invested a lot in the development of high quality zeolites that led to the discovery of the famous Zeolite Socony Mobil-5 (ZSM-5). Like other crystalline aluminosilicates with an alumina tetrahedron constructions that are supported by oxygen connections, ZSM-5 is highly active catalyst in petrochemical reactions. High surface area, solid acidity, thermal and chemical stability and structural pores are some of the features that make these aluminosilicates active catalysts (Cundy and Cox 2003).

Catalysts employed in catalytic cracking should be robust and highly competitive due to the ever-changing feedstock. Pyrolysis oil emanates from thermal decomposition of biomass in a non-oxygenated environment to produce liquid (bio-oil), gases, and solids (Domínguez-Barroso *et al.,* 2016)**.** The Physio-chemical setup and orientation of pyrolysis bio-oil is: high oxygen and moisture content (Veses *et al.,* 2015), low heating values, poor chemical and thermal stability compared to crude oil (Liu, Yan and Chen 2013)**.** Additionally, Zhao *et al.*, (2014); Zheng *et al.*, (2014); reported corrosive nature of bio-oils, attributed to their pH that is in the range of 2-3.

Just like vegetable oils, bio-oils require upgrading to meet fuel criteria as hydrocarbon fuels. ZSM-5 has been used in catalyst composites and as a catalyst to produce light olefins (Ahmad *et al.,* 2016), upgrading pyrolysis vapours by reducing viscosity, acidity and oxygen content (Veses *et al.,* 2015), in aromatization of hydrocarbons and oxygenated organics (Nash, Dry and O'Connor 1996; Fang *et al.,* 2010; Mante *et al.,* 2014; Mohiuddin *et al.,* 2016), catalytic cracking (Corma *et al.,* 2007; Mante *et al.,* 2014; Zhao, Wei, Cheng, Cao *et al.,* 2015; Ahmad *et al.,* 2016). ZSM-5 amongst other materials has been reported to be an active and good support material for upgrading bio-oils. Shape selectivity, ion-exchange properties and pore structure and such as tri-dimensional micro-pore topology and large specific surface area in ZSM-5 are typical characteristics of this material that make it a favourable catalyst (Rahimi and Karimzadeh 2011).

There is a wide spectrum of the application of ZSM-5 based catalysts and vegetable oil as a source of energy in literature. A closer attention has been paid to ZSM-5 based catalyst in many chemical transformations because the type of zeolite applied has the main influence on the product distribution. Recently, upgrading bio-oils to usable liquid fuel that has properties similar to petroleum liquid fuels has been one of the current research areas. The main methods in the liquid fuel production from bio-oil have been hydro de-oxygenation (Vitolo *et al.,* 2001) and heterogeneous catalytic cracking (Krár *et al.,* 2010); with catalytic cracking being the main method, considerations for catalysts is that they must be highly efficient, selective (Ishihara *et al.,* 2015) and eligible for regeneration (Zhao, Wei, Cheng, Cao *et al.,* 2015). These properties are owed to chemical and thermal stability of catalyst materials applied in the bio-oil upgrading. In the petrochemical industry, a series of challenges such as catalyst deactivation, poisoning, coking and poor selectivity make catalyst choice a crucial factor. ZSM-5 found a wide application in chemical reaction engineering. Better catalytic activity and selectivity towards light olefin was observed when ZSM-5 was compared with H-MOR, H-BEA and USY zeolites. Deactivation due to carbon deposition was also not as pronounced as in the other three zeolites that were studied (Luo *et al.,* 2014). Cracking is one of the most important steps in the petrochemical industry, this because the feedstocks are composed of long chain molecules. In this study, the biomass-derived oils are used as feedstock. These oils are composed of high molecular weight that also contain long chain fatty acid (Wu, Rodgers and Marshall 2004). Large molecules cannot perforate through the pores of the catalysts resulting in coke formation and deactivation. The versatility of ZSM-5 is commendable, this material can be synthesised with customised morphology aimed to increasing perforation efficiency with meso to macroporosity and enhancing selectivity toward valuable chemicals (Garcia-Martinez *et al.,* 2014; Qi *et al.,* 2017). ZSM-5 was also reported to form highly active composites with other materials such as MCM-41, SBA-15 and SAPO-34 amongst others (Ji, Yang and Yan 2017).

CHAPTER 3

3. Methodology and procedure

3.1 Methodology

The conversion of canola oil over promoted HZSM-5 based catalysts was studied using a three stages experimental approach. The three stages were: 1) Synthesis of hydrocarbons without using a catalyst. 2) Synthesis of hydrocarbons using an unpromoted HZSM-5 sample. 3) Synthesis of hydrocarbons using promoted HZSM-5 samples.

The samples were promoted by loading them with either Ni or Sn using $NiCl_2{\cdot}6H_2O$ for Ni loading, and $SnCl_2$ for Sn loading (Details of promotion techniques outlined in sections 3.1.3-5.). The synthesis of the hydrocarbons was carried out in a ½ inch stainless reactor. In all cases a Weight Hourly Space Velocity of 10.6 hr^{-1} was maintained using an HPLC pump.

3.1.1 Equipment and apparatus

To successfully complete the experimental work in this study, the following equipment and apparatus were to prepare both the catalysts and conversion products:

- Muffle furnace
- Oven
- Hollow Tube Furnace
- HPLC pump
- Reactor
- Round bottom flasks.
- Gas collectors

Catalyst and product characterization techniques:

- X-Ray Fluorescence Spectrophotometer (Axios PAnalytical)
- Gas chromatography-mass spectrometry (Shimadzu GC-MS QP 2010 Ultra)
- Gas chromatography-flame ionization/thermal conductivity detectors (Shimadzu GC-FID/TCD 2014)

Figure 4, below show the schematic representation of the experimental methodology carried out in this study:

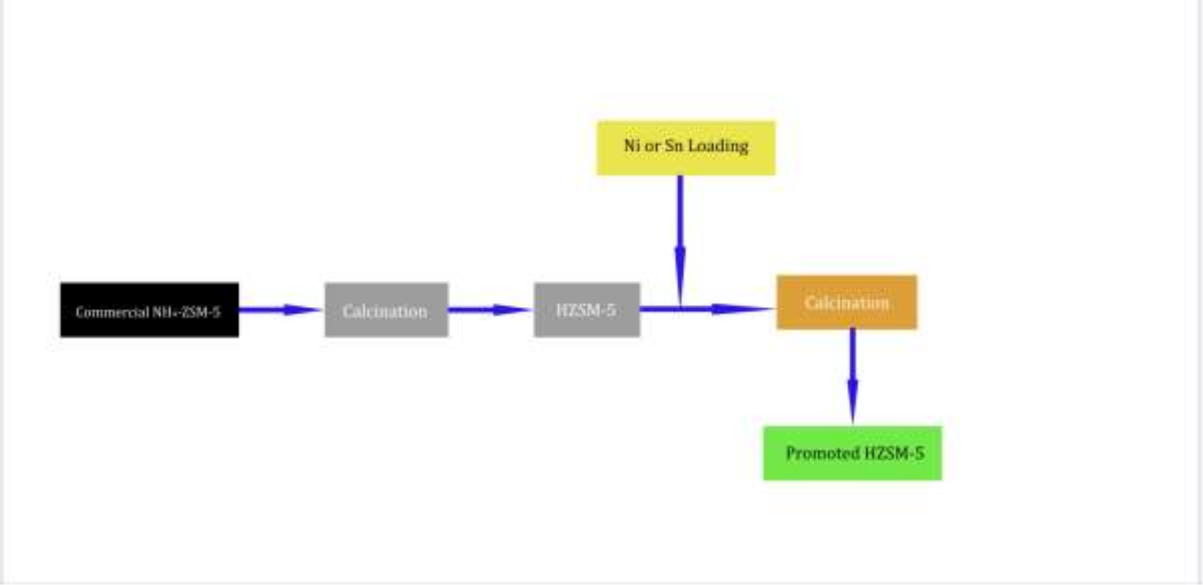


Figure 4, Experimental procedure flow-chart

In this work, canola oil was converted to hydrocarbons using thermo-catalytic processes. To study the effect of HZSM-5 based catalyst on the products that emanate from the reactor, the same sample of HZSM-5 was used in all promotions. The bulk of the sample was calcined to obtain the parent HZSM-5. After the parent (unpromoted sample) was obtained, the preparations followed as outlined in sections 3.1.3 to 3.1.5.

3.1.2 Catalyst preparation

In this work, a total of 16 zeolite samples were tested in the conversion of canola oil. The first sample preparation was the calcination of the commercial NH_4-ZSM-5 zeolite with a Si/Al ratio of 50 at 550 °C for 3 hours. From the commercial zeolite, 15 samples were prepared using three techniques; incipient wetness promotion (IW), aqueous solution promotion (AQ) and mechanical mixing promotion (MM) to load Ni and Sn on HZSM-5. For each technique, a series of targets of 0.5%, 1%, 3%, 5% and 7% samples were prepared for each cation i.e. Ni and Sn using $NiCl_2.6H_2O$ for Ni-loaded samples and $SnCl_2$ for Sn-loaded samples. In all case analytical grade chemicals up to 99.9% purity were used to avoid impurities during catalyst preparations.

3.1.3 Incipient wetness promotion

To load the cations on the unpromoted HZSM-5 using the IW technique, the required amount of salt was dissolved in an experimentally determined volume of water making a solution that is used to wet the calculated amount of zeolite solid sample dump. The solution was thereafter added to the solid slowly to ensure that it wets the solid evenly. The wet solids were covered and stood for 3 hours then dried in the oven for 3 hours at 105˚C and calcined at 550˚C for 3 hours in a muffle furnace. After calcination, the samples were thoroughly homogenized with mortar and pestle.

3.1.4 Aqueous solution promotion

Cations were loaded on the unpromoted HZSM-5 by dissolving the required amount of salt in water 50 times the weight of the solid sample. The mixture was stirred for 3 hours. The water was evaporated gently using a hot plate. After the samples were almost dry, it was dried in the oven for 3 hours. The samples finally calcined at 550˚C in a muffle furnace for 3 hours. After calcination, the samples were thoroughly homogenized with mortar and pestle.

3.1.5. Mechanical mixing promotion

Mechanical mixtures of HZSM-5 and salts of the required weights were prepared by mechanically mixing the materials with mortar and pestle. After mixing, the samples were made to stand for 3 hours, and then dried in the oven for another 3 hours. The samples were thereafter calcined in a muffle furnace at 550˚C for 3 hours. After calcination, the samples were thoroughly homogenized with mortar and pestle.

3.1.6 Percentage loading

In this this work, % loading is expressed as wt. % of the metal cation to the sum of the cation and zeolite weight. % loading = stoichiometric weight of the metal in the amount of salt used ÷ (weight of the Zeolite + stoichiometric weight of the metal in the amount of salt used. Knowing the atomic weights of Ni and Sn, 58.69 and 118.71g/mol respectively, the mass fraction of the cation, X_{cation}, can be calculated for each salt.

3.2 Catalyst activity tests

Ultimately, the catalyst's activity is expected to produce feed chemical derivatives, and or chemical transformation of the feed molecules. Several reactions including but not limited to: deoxygenation (Lovás *et al.*, 2015), cracking (Gong *et al.*, 2011), aromatization (Tshabalala and Scurrell 2015), decabonylation (Wang, Kim and Brown 2014) and decarboxylation (Melligan *et al.*, 2013) are known to take effect during thermo-catalytic conversion of BDO's over ZSM-5 based catalysts. It is through some of these reactions that certain products were achieved. To study the catalytic activity, the product stream of the prepared (loaded) samples were compared to the products of pyrolysis i.e. heating without a catalyst, and also compared to the products of the unpromoted commercial HZSM-5. The activity was evaluated based on the products obtained, their distribution and fractional conversion of the feed. *Figure 5*, below, outlines the steps followed to carryout catalyst tests:

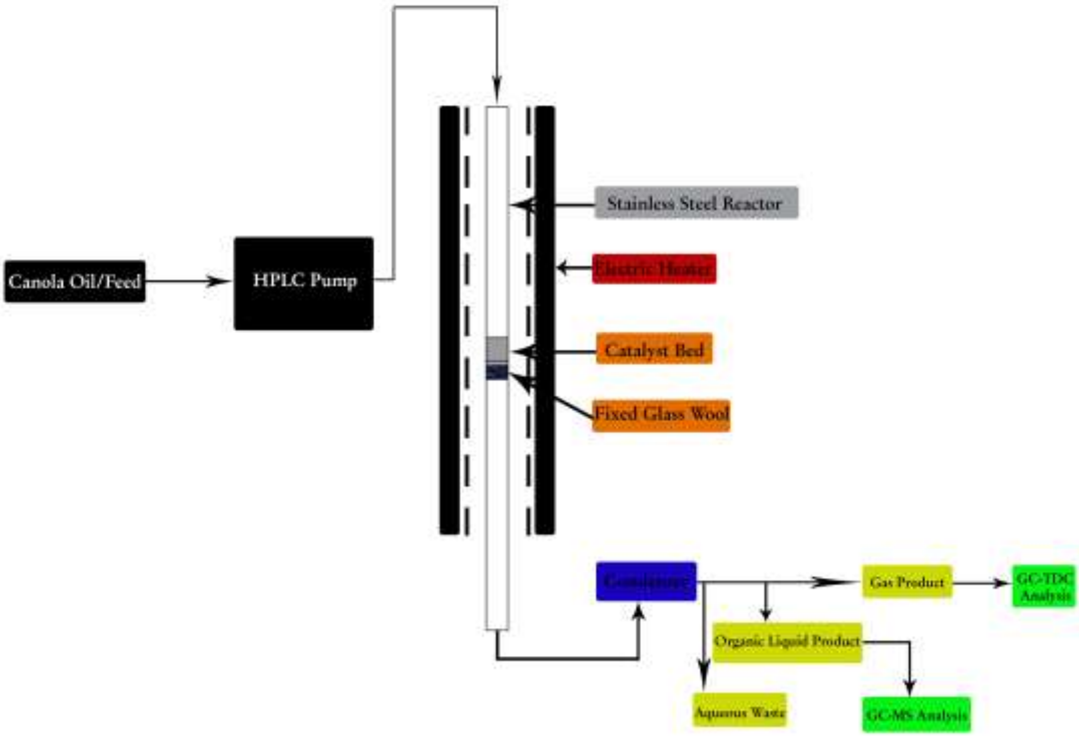


Figure 5, Experimental scheme for the conversion of Canola oil over HZSM-5 based catalysts

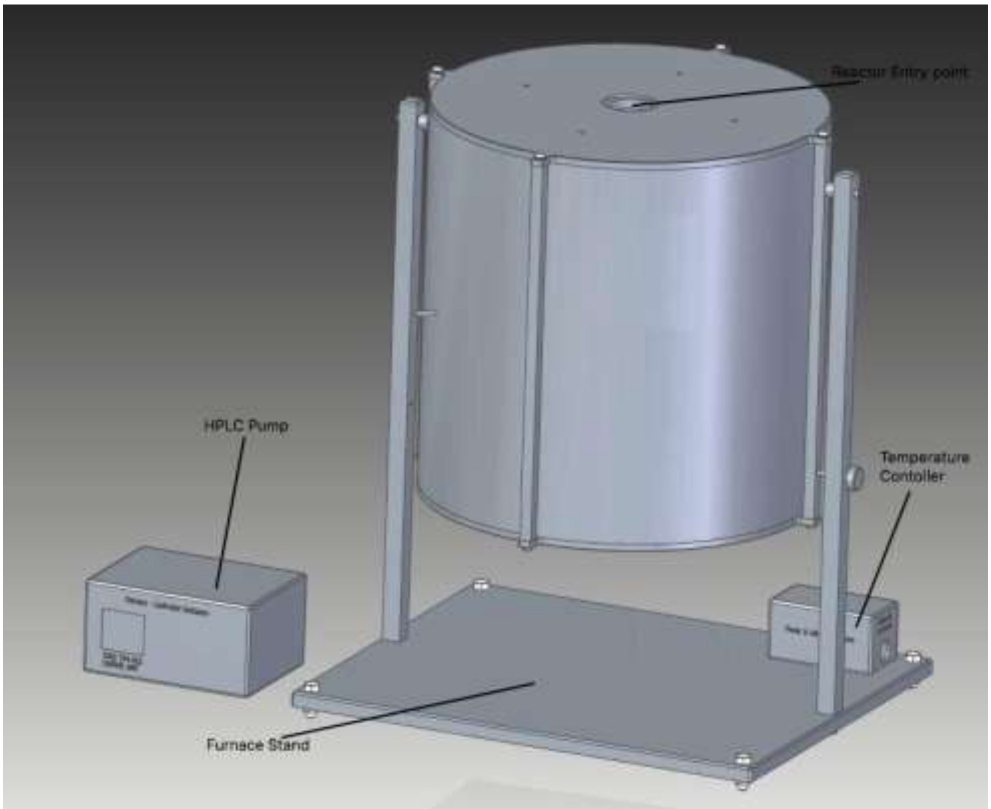


Figure 6, Solid Edge illustration of the furnace

Some of the main features of the setup include an air tight container for the Canola oil with a fully immersed HPLC pump suction to ensure that the pump does not draw air. A tube furnace fitted with a temperature controller to maintain ~450 °C. The furnace was heated to the desired temperature and maintained for 35 minutes. Additionally, glass wool was used to insulate the system by blocking the spaces between the walls of the furnace and the reactor. A solid edge pictorial representation of the furnace is shown in *Figure 6* for ease of reference. The feed was fed at a WHSV of 10.6 hr^{-1} for 4.5 hours to obtain a representative sample of the gas and liquid products.

CHAPTER 4

4. Results and discussion

This chapter couples the results and background knowledge to interpret the findings of the work based on the characterisation of products using GC-TCD and GC-MS. The characterization of products obtained from the synthesis of hydrocarbons using unpromoted HZSM-5, and Ni and Sn-HZSM-5 from canola oil to the gas and organic liquids were studied. The feed (canola oil) was converted varying the samples' metal concentration using the target 0.5, 1, 3, 5 and 7% loading.

In all cases, the WHSV and temperature of the reactor were kept fairly constant at 10.6 hr^{-1} and 450˚C respectively. Two comparative tests were also done using an unpromoted HZSM-5 and a non-catalysed condition. There are two general areas considered in this chapter, namely; a) qualitative identification of synthesized products and eventually b) Selectivity and product distribution, products and their applications.

4.1.2 XRF characterization of loaded samples

To confirm that loading was accomplished, Wavelength Dispersive X-ray fluorescence spectroscopy (WDS) was used to quantify Ni and Sn ions in the HZSM-5 samples that were used in the study. The cation composition was used to discuss the degree of loading of the 3 different techniques used. It was observed that the loading efficiency followed the order: IW<MM<AQ for both Ni and Sn, as tabulated in *Table 5* below. Blanks, duplicates, and reference materials were used to ensure quality of the reported data on WDS. A calibration with a correlation coefficient of 0.99837 was achieved.

Figure 7, some of the pressed pellets and reference materials for %Sn and Ni composition analysis on WDS

Table 5. Elemental analysis of HZSM-5 and Ni and Sn-HZSM-5 samples

Nickel Promoted Samples		**Tin Promoted Samples**	
	XRF Ni (%)		**XRF Sn (%)**
AQ 0.5	0.10	AQ 0.5	0.10
MM 0.5	0.14	MM 0.5	0.25
AQ 1	0.16	IW 0.5	0.31
MM 1	0.18	AQ 1	0.36
IW 0.5	0.19	MM 1	0.43
IW 1	0.41	IW 1	0.54
MM 3	1.24	AQ 3	0.95
IW 3	1.28	AQ 5	1.63
AQ 3	1.33	MM 3	1.77
AQ 5	1.47	IW 3	1.86
MM 5	1.61	MM 5	2.73
IW 5	1.92	IW 5	2.99
AQ 7	2.14	AQ 7	3.13
MM 7	2.69	MM 7	3.82
IW 7	3.00	IW 7	4.27

To compare the promotion techniques and loading efficiency, *Figure 8* below, shows the relationship between the calculated (sample preparation values) were plotted with XRF values.

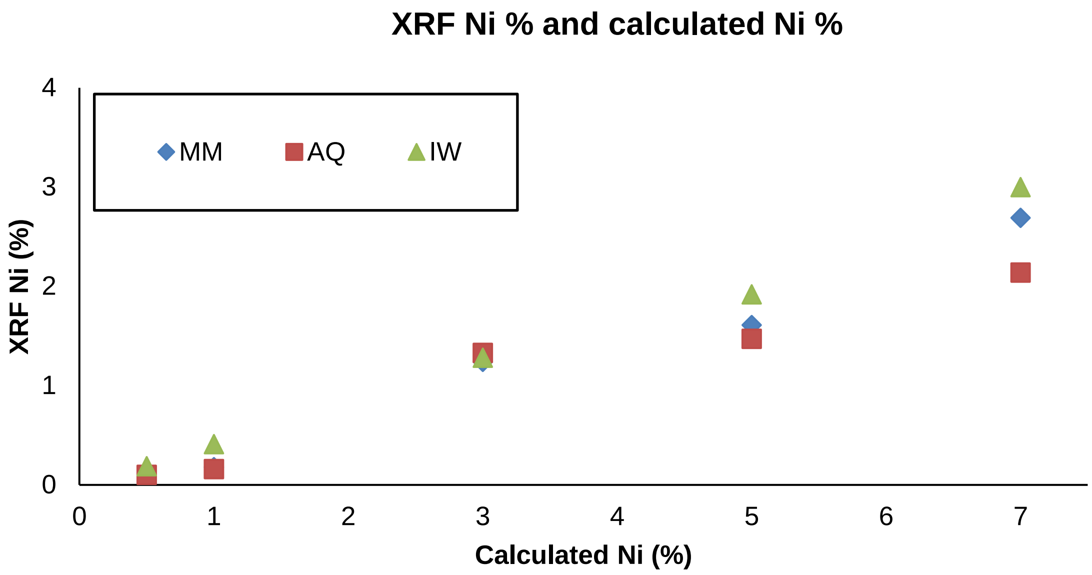


Figure 8, XRF % composition of Ni vs calculated % Ni composition

The plots in *Figure 8* yielded the equations given below using regression analysis to show the loading efficiency of different techniques for Ni-loading:

$Y_{IW} = 0.4196x - 0.0248$ with $R^2 = 0.9937$, $Y_{AQ} = 0.3144x + 0.0024$ with $R^2 = 0.9392$ and $Y_{MM} = 0.3863x - 0.1028$ with $R^2 = 0.9774$

In all cases, the coefficient of determination R^2 is reported to show the portion of the variance in the XRF cation % for Ni and Sn. For Ni, the data correlates with a minimum of 93.92% for AQ 97.74% for MM and 99.37% for IW. The slope gives the numerical value for loading efficiency. The regression gives conclusion that the order of loading efficiency assumes IW, 41.96%; MM, 38.63% and AQ 31.44%.

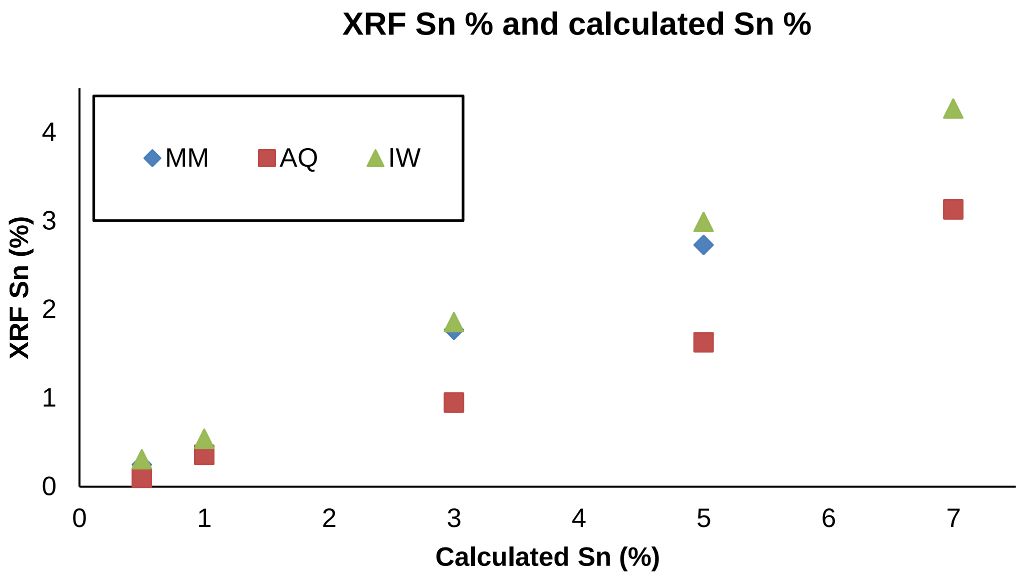


Figure 9, XRF % composition of Sn vs calculated % Sn composition

The plots in *Figure 9* yielded:

$Y_{IW} = 0{,}6112x - 0{,}023$ with $R^2 = 0{,}9993$; $Y_{AQ} = 0{,}4349x - 0{,}2011$ with $R^2 = 0{,}9581$ and $Y_{MM} = 0{,}4699x + 0{,}1114$ with $R^2 = 0{,}9648$

For Sn, the data correlates with a minimum of 95.81% for AQ, 96.48% for MM and 99.93% for IW as a maximum. Similar to Ni, the slope gives the numerical value for loading efficiency. The regression gives conclusion that the order of loading efficiency assumes IW, 61.12%; MM, 46.99% and AQ 43.49%. From this data, it can be concluded that the loading efficiency is more pronounced for Sn than it is for Ni. With reference to promotion techniques, the order of efficiency assumes IW>MM>AQ in all cases. Looking at the methods the higher loading efficiency for the MM technique can be assigned to the fact that little to no material was lost due to transfer because the precursor was added to the HZSM-5 without dissolving it first. In the case of the low AQ efficiency, the amount of solvent used was the most in comparison to the IW technique.

Table 5, *Figure 8*, and *Figure 9* show the loading as the WDS results show that detected wt. % of Ni and Sn increased with the amount of the salt added for all the techniques. This suggests that the cations were detected in the samples and loading is confirmed by XRF. Despite analytical calculated quantities added to samples, the amounts of cations detected was not equal to the calculated (target) concentrations this can be attributed to possibility of ion exchange in the samples, loss of part of the sample and inhomogeneity. The tables also show that the highest target 7%, Ni-loaded sample read 3.00% loaded by IW as compared to 7% Sn-loaded sample that read 4.27% also loaded by incipient wetness promotion.

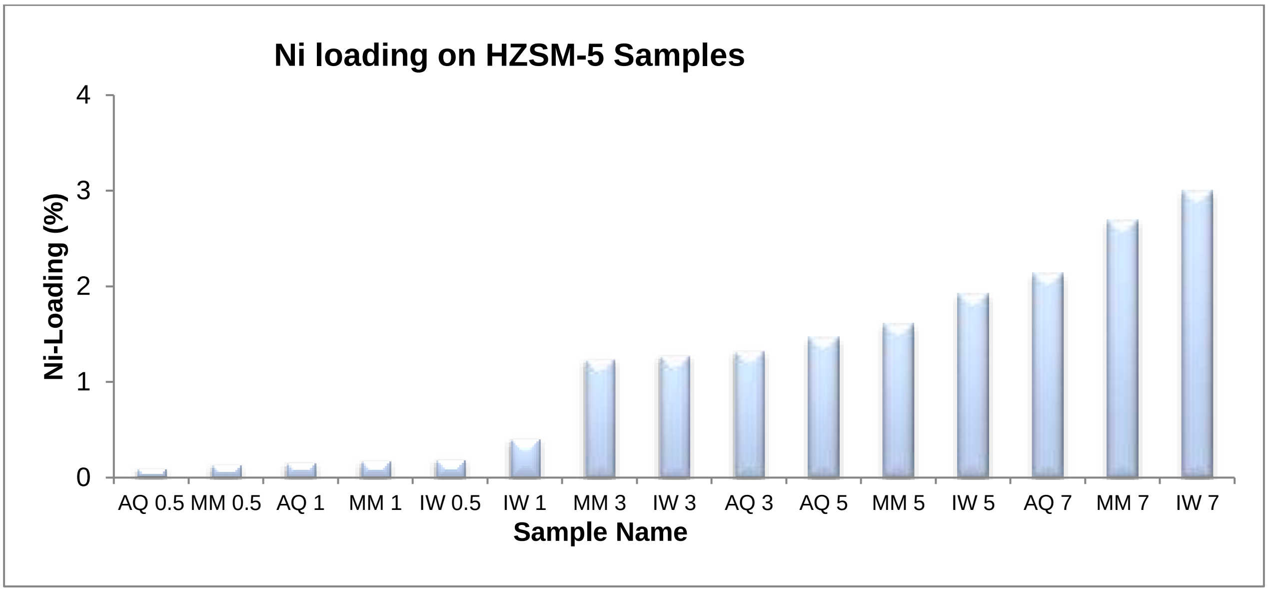


Figure 10, XRF % composition of Ni-Loaded samples

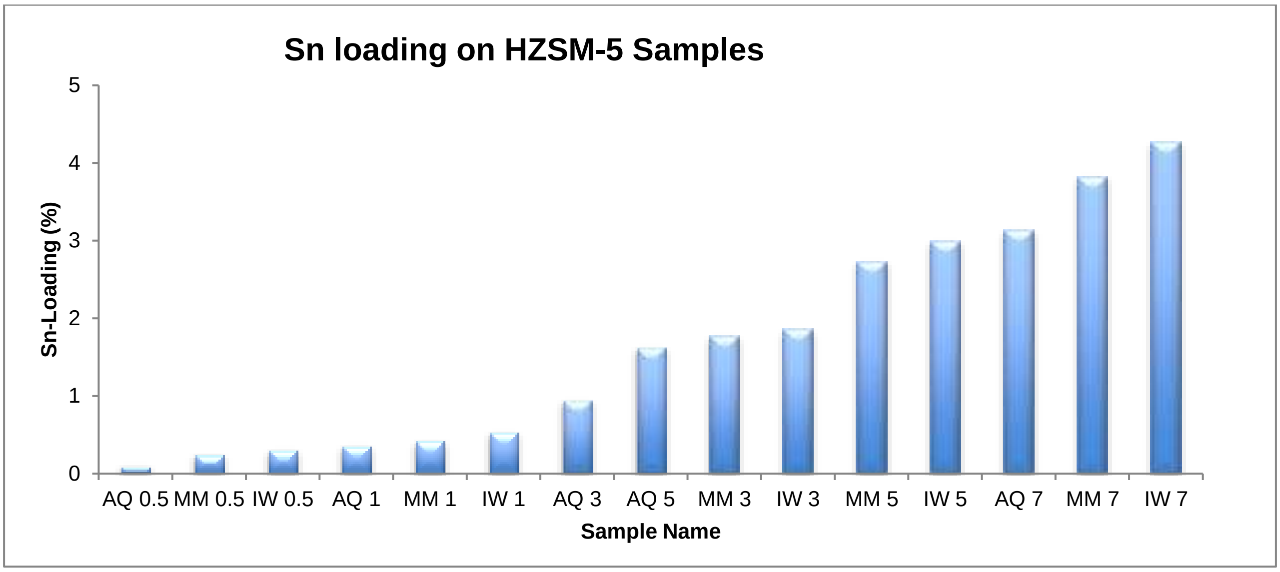


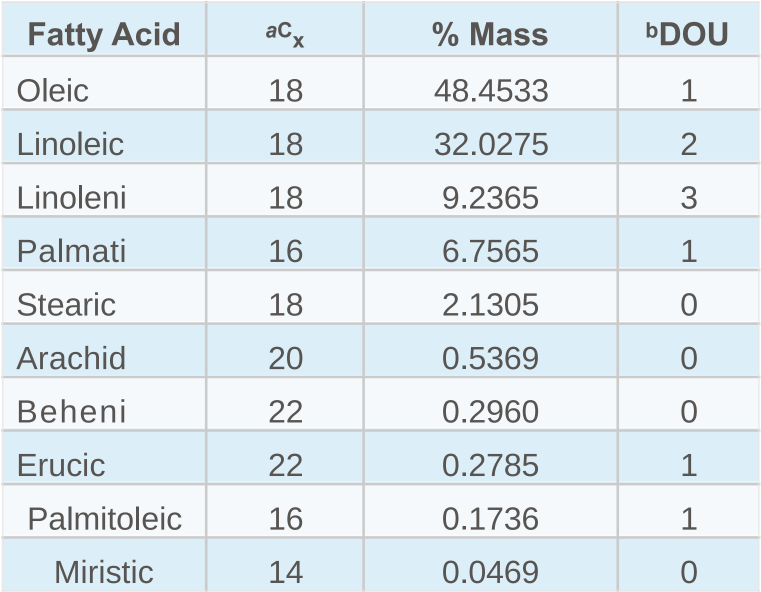
Figure 11, XRF % composition of Sn-Loaded samples

Figure 10 and *Figure 11* show the ascending arrangement loading as presented by WDS. The obtained results will be used throughout this work. The arranged order of increasing loading for both Ni and Sn is presented to indicate the range of cation concentration for ease reference. As expected, the cation concentration increases as experimentally targeted, however the actual loading reported by WDS is lower than the target. This could be due to the fact that the samples were not well homogenized as they were not in large quantities for the pulverisers but rather homogenized with mortar and pestle.

4.2 Feed characteristics

Characterization of vegetable oils as reported in literature where compared with that of the canola oil used in this study. There is not a significant difference. The main constituents of vegetable oils are the C_{18} fatty acids such as: oleic acid, linoleic acid and stearic acid to mention some. Canola oil composition is dominated by single double bond oleic acid and a 2 double bond linoleic acid in its composition. There are also traces of palmitic acid (C_{16}), stearic acid (C_{18}) and linolenic acid (C_{18}). *Table 6* shows the fatty acid composition of canola oil showing oleic and linoleic acids as the major components.

Table 6. The typical fatty acid composition of canola oil (Batista et al., 1999)



Fatty Acid	$^{a}C_{x}$	**% Mass**	^{b}**DOU**
Oleic	18	48.4533	1
Linoleic	18	32.0275	2
Linoleni	18	9.2365	3
Palmati	16	6.7565	1
Stearic	18	2.1305	0
Arachid	20	0.5369	0
Beheni	22	0.2960	0
Erucic	22	0.2785	1
Palmitoleic	16	0.1736	1
Miristic	14	0.0469	0

Gas Chromatography Flame Ionization Detector, (GC-FID) with a ZBFFAP polar column, was used to confirm the presence of fatty acids, the feed was sampled and analysed using a mixture of standards of known concentration. An analysis of the retention time revealed the presence of oleic acid at 45.7375%, linoleic acid 27.3561, and palmatic acid at 5.2374%. Other unidentified components were observed. This work investigates the synthesis of hydrocarbons from the fatty acids present in the feed (Canola oil). At this junction, the reaction feed is then recognized as a stream rich in the main fatty acid components of the oil that are converted to the products that emanate from the reactor as characterized by the GC-MS.

Table 7. GC-FID fatty acid composition of Canola oil

Fatty Acid	$^{a}C_x$	**% Mass**	^{b}**DOU**
Oleic	18	45.7375	1
Linoleic	18	27.3561	2
Palmatic	16	5.2374	1
Other	16	21.6690	-

$^{a}C_x$ = Number of carbon atoms in fatty acid

^{b}DOU = Degree of unsaturation represented as the number of double bonds in the fatty acid

The tables above show that the major fatty acids in canola oil, oleic and linoleic acid are those that have double bonds, making them easier to crack due to unsaturation as compared to saturated fatty acids such as stearic, arachidic, behenic and miristic acid.

4.3.1 The effect of HZSM-5 catalyst on the product obtained

The role of the catalyst was to facilitate the production of value added products from the feed. Since non-catalytic tests were compared to catalysed tests to observe the effect of the catalyst on product distribution, selectivity and yield, it is assumed that the difference was entirely due to the introduction of the HZSM-5. This assumption was based on the fact that the other variables such as temperature ~450°C, pressure (atmospheric) and feed flowrate were kept constant. Catalytic conversion of canola oil over unpromoted HZSM-5, *Table 9*, was compared with the passing of canola oil through the reactor without any zeolite sample, referred to as pyrolysis *Table 8*. The GC-MS product characterizations revealed that the employment of the HZSM-5 catalyst has facilitated the chemical transformation of the feed from oxygenates (fatty acids) to mainly de-oxygenate; i.e. hydrocarbons in a diverse and wide spread class of chemical identities such as: aromatics, cycloalkenes, alkenes, alkanes, and aromatics to mention a few.

Table 8. GC-MS characterization of oxygenates of the pyrolysis of canola oil at 450℃, WHSV 10.6 hr^{-1}

Mass %	Product Name
0.76	10-Undecenoic acid, octyl ester
0.82	n-Decanoic acid
1.97	Pentadecanoic acid
1.19	Z-(13,14-Epoxy)tetradec-11-en-1-ol acetate
0.83	10-Heneicosene
46.74	cis-Vaccenic acid
15.31	17-Octadecynoic acid
4.15	Octadecanoic acid
2.33	cis-9-Hexadecenal
3.41	9-Octadecen-1-ol, (Z)-
1.11	9-Octadecen-1-ol, (Z)-
1.37	Ethanol, 2-(9,12-octadecadienyloxy)-, (Z,Z)-

The complete GC-MS results are attached in the appendix. In the two earlier tables, it is shown that the role that the catalyst plays is not limited to the product distribution but also includes conversion. One of the evident effects of a higher WHSV is the detection of higher mass fractions of the 18-carbon organic acids, i.e. cis-vaccenic acid, octanoic acid and cis-9-hexadecenal, (an aldehyde that may result in the reduction of the initial carboxylic acids) that were detected in the product. Additionally, there are fractions of alcohols and acetates that show a lower deoxygenation capacity at 450°C thermal conditions. However, the HZSM-5 sample product as shown in *Table 9* shows that HZSM-5 has increased the fractional conversion of the reaction evident through the absence of the C_{16-18} carboxylic acids that were fed.

Table 9. GC-MS characterization of aromatic products that emanate from the HZSM-5 thermo-catalytic conversion of canola oil at 450℃, WHSV 10.6 hr^{-1}

Mass %	Product Name
6.00	Benzene
13.43	Toluene
5.01	Ethylbenzene
2.17	o-Xylene
1.88	o-Xylene
1.94	Benzene, propyl-
1.56	Benzene, 1-ethyl-3-methyl-
1.13	Benzene, 1-ethyl-3-methyl-
1.31	Benzene, 1-ethyl-3-methyl-
1.15	Benzene, butyl-
2.32	2-Methylindene
5.14	Azulene
2.13	Naphthalene, 1-methyl-

After the introduction of the unpromoted HZSM-5, the formation of aromatic hydrocarbons was observed as shown above. The production benzene and its derivatives such as toluene, o-Xylene and other compounds was enhanced as show above. In this work, a higher WHSV of 10.6 hr^{-1} was chosen by increasing a faster flowrate as this is mainly important for the consideration of upscaling projects. Another option would be to use large amount of catalyst and a relative and maintain a lower flowrate. Unfortunately, catalysts are usually expensive materials. It is for this reason that the relatively high WHSV was considered.

In order to establish the material balance around the system, weight analysis was done as follows:

- The mass of the feed and OLP containers were measured before and after the reaction and the change in mass was reported as the feed mass and product mass respectively.
- The mass of the produced coke/ char was obtained calculating the difference in the initial mass of the catalyst and that of the spent catalyst.

- The mass of the gas product was expressed as the difference between the amount of feed and the sum of coke/char and OLP.

The gas composition was characterized by GC-TCD and the yield of each fraction was determined. The GC-MS was used to characterize the liquid fractions of the products to study of catalytic properties such as: de-oxygenation and aromatization, conversion and product distribution in the liquid fraction of the products. Notably, to quantify the different products in the OLP, the area percentages of the peaks from the chromatograms were used to report the mass percentages.

For the gas products there were no significant composition variation with the detected species and their concentration that were qualified using retention time by comparing with a sample of mixed standard gases of known concentration. Some of the notable observations were that the gas product mixture constituted of CO_2, CO, CH_4. *Table 10* below shows an analysis of samples Ni-MM 1, Sn-MM 5, Ni-AQ 3, Sn-AQ7, Ni-IW 0.5 and Sn-IW 1 as examples:

Table 10. GC-TCD gas product analysis

	CO_2 (%)	**CO (%)**	**CH_4 (%)**
HZSM-5	15.2321	6.1254	11.4242
Ni-MM 1	15.3732	5.2318	9.8927
Sn-MM5	14.9821	5.1089	10.0127
Ni-AQ 3	15.6326	5.1263	10.0081
Sn-AQ7	14.8928	5.1731	9.9898
Ni-IW 0.5	15.1256	5.1212	10.0702
Sn-IW 1	14.8899	5.0971	10.0079

From *Table 10*, it is evident that the selectivity in the gas fraction is not influenced by the composition of the HZSM-5 based samples and the results show a mean of difference within ±1.0%. This may be attributed to the fact gas molecules are generally smaller in size than liquid molecules. The zeolite material at constant temperature and WHSV had a constant degree of gas products produced probably because the pore sizes and volume is at a size that could not segregate the range of gas products from cracking. This discussion is based on the assumption that the system selectively produces certain products based on molecular sizes as a molecular sieve. Only a certain cut-off size may pass through the catalyst bed to form products, otherwise, such fraction of the feed with emerge unconverted, this will referred to as *"Conversion-OLP relationship"*. In essence, the lower the conversion, the more the OLP yields because the feed is essentially a liquid; the higher the conversion, the lower the OLP yield. The results on the yield of OLP, Gas and Coke are assumed to be independent of the effect of pore sizes based on the fact that the Sn loading reduces OLP as the loading increases while Ni loading increases OLP as loading increases as shown in *Figure 13* and *Figure 14*. These two observations are contradictory, hence, validating that the OLP/Gas yield is probably independent of pore size. Based on this observation, it can be also be concluded that the OLP yield also increases with low conversion as observed in

Table 11 and *Figure 13* satisfying the assumption *Conversion-OLP relationship* assumption.

4.3.2 The effect of metal loading on the catalytic conversion of BDOs to hydrocarbons and fuel range chemicals

Two metal cations (Ni and Sn) were added to the unpromoted catalyst using chlorides as the sources of cations. Three different methods, namely Aqueous Promotion, Incipient Wetness Promotion and Mechanical Promotion, were used to load the cations on the unpromoted HZSM-5. The loading assumed cation values between 0.1 and 4.27% by weight.

In this work, the target general chemical reaction is the de-oxygenation of the feed, to produce hydrocarbons such as aromatics, alkanes and alkenes. In order to study the effect of loading on conversion, the mass fraction of components originally in the feed that emanate in the product was assumed to indicate the fraction of the feed that did not convert chemically. In turn, the detected compounds by GC-TCD and GC-MS were used to calculate conversion under this assumption. Fractional conversion is the portion of the feed that reacted expressed as the ratio to the amount that was fed.

$$Conversion = Moles_{in} - Moles_{out} \div Moles_{in}$$

At this junction, it is worth noting that in the moles referred to in the conversion equation are the moles of the C_{16-18} fatty acids. The quality of the product as a fuel range is classified based on the mass fractions of the $C_4 – C_{12}$ range hydrocarbons (light hydrocarbons) against the mass fractions of oxygenates (low calorific value compounds) in the product. The study looked at conversion products referred to as catalytic conversion. Catalytic conversion outlines the identity of the conversion products, i.e., hydrocarbon classification as straight chains, aromatics, oxygenates etc. During the chemical reaction, the feed was converted to products, distributed in the gas, liquid and solid (coke) products. The gas fractions contained CO, CO_2, CH_4 and unidentified gases.

To quantify conversion the amount of C_{16-18} carboxylic acids in the products was converted to assumed to represent the fraction of the feed that was not chemically converted then this quantity was subtracted from $Moles_{fed}$ calculated by the mass of feed ÷ 887g/mol where 887g/mol is the molecular mass of canola oil.

The conversion ~1, which is 100% for all the tested Ni-loaded samples, no fatty acids where detected in the OLP. Since C_{18} fatty acids are liquids at room temperature, it was concluded that the amount of C_{18} fatty acids in the gas product was zero. These results suggest that the loading of Ni the HZSM-5 samples had no effect on fractional conversion, also in agreement with the earlier assumption of *Conversion-OLP relationship*. *Table 11* shows the effect of Sn-loading of the fractional conversion.

Table 11. Product franction by chain length and fractional conversion for Sn-loaded HZSM-5 samples

Sample	C6 (%)	C7 (%)	C8 (%)	C9 (%)	C10 (%)	C12 (%)	C16 (%)	C18 (%)	Conversion (%)
Sn-MM 0.5	4.03	17.29	40.02	20.37	8.85	3.42			~100
Sn-MM 1	5.27	14.74	47.36	21.21	5.97	1.68			~100
Sn-MM 3	4.60	21.01	40.66	24.33	8.11	1.08			~100
Sn-MM 5	3.32	13.34	29.57	21.36	5.42	0.97	2.33	14.20	91.40
Sn-MM 7	0.00	9.24	18.37	14.06	3.16		5.72	37.70	77.90

The conversion of Canola at higher WHSV is low 65.2%, however when the HZSM-5 Catalyst was introduced, the conversion was lifted to ~100. The same was observed for all the Ni-loaded (Ni, atomic radius = 135pm) samples. The components detected in the OLP were mainly shorter than the initial C_{16-18} present in the feed. When the HZSM-5 was loaded with Sn (atomic radius = 145pm), at higher loading %, the conversion was lowered up to 77.9%. The unreacted components of the feed were mainly the C_{18} than C_{16} carboxylic acids, refer to the chromatograms in the appendices A6 and A7, this observation is in agreement with the idea that longer chain molecules have a higher cracking activation energy (with reference to cracking reactions) as compared to shorter chains (Ahmad *et al.,* 2016).

4.3.3 The effect of metal loading on product distribution during the catalytic conversion of BDOs to hydrocarbons.

The chemical reactions in the reactor produced more than one product. The product distribution was studied by evaluating the ratio of individual products to others expressed as a percentage. Since the products were many, the percentage composition of products produced was considered for groups of related products. *Figure 12*, below shows the scheme of the products.

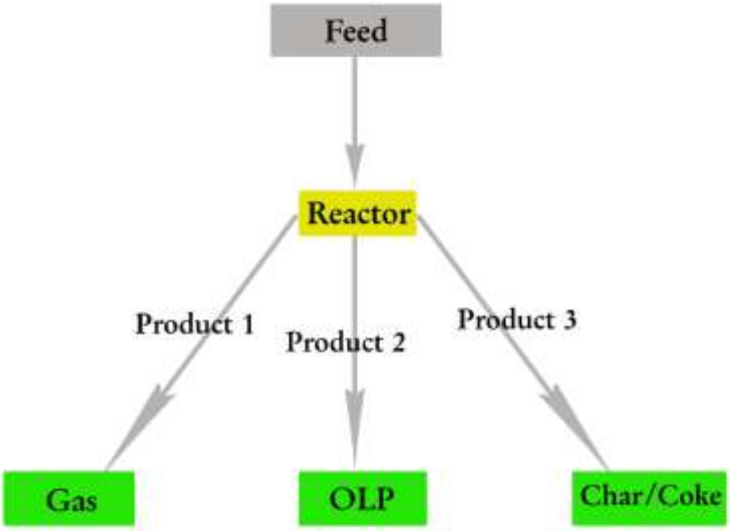


Figure 12, Product distribution schematic concept map for HZSM-5 based samples at 450℃ and WHSV of 10.6 hr^{-1}

The product distribution was considered for the three obtained products in the testing of the promoted samples; coke/char, OLP and gas products. The results show that the metal loaded on the HZSM-5 by different promotion techniques has an effect on the proportions of the gas-liquid-coke percentages.

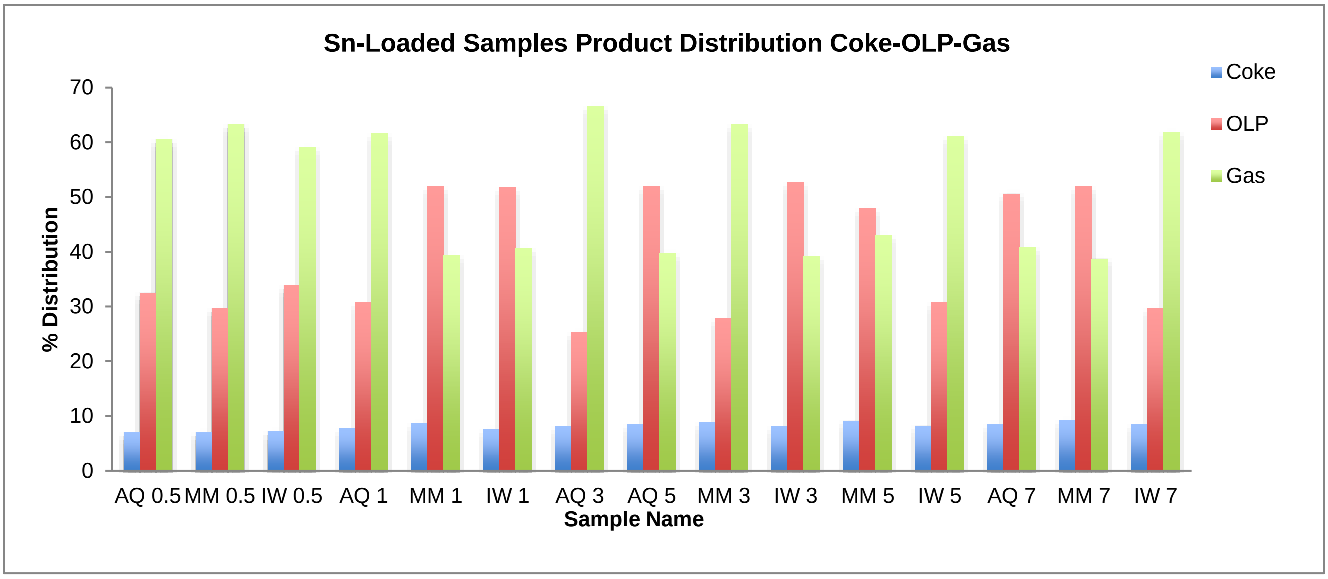


Figure 13, Coke, OLP and Gas product distribution of the Sn-promoted samples at 450℃, WHSV of 10.6 hr^{-1}

From *Figure 13*, the OLP distribution shows a non-linear increases with increasing Sn-promotion from a minimum of 32.5% to a maximum of 52.0% and flattens by 51.9 and 50.6% for AQ 0.5 – AQ 7, and increases from a minimum of 29.6% to a maximum of 52.7% for the IW 0.5 - IW 3, drops down to 33.8% for the IW 3 – IW 7. The highest observed OLP yield was 52.7% for IW 3 and the lowest was 29.6% for IW 0.5. An overall periodic behaviour was also observed for the MM 0.5 – MM 7 samples between the period minima; 29.6% and 27.8% and two 52.0% maxima OLP. The coke formation was on an overall increase as the Sn-promotion increased without exceeding 1% ranging from 7.0154 to 9.2755%.

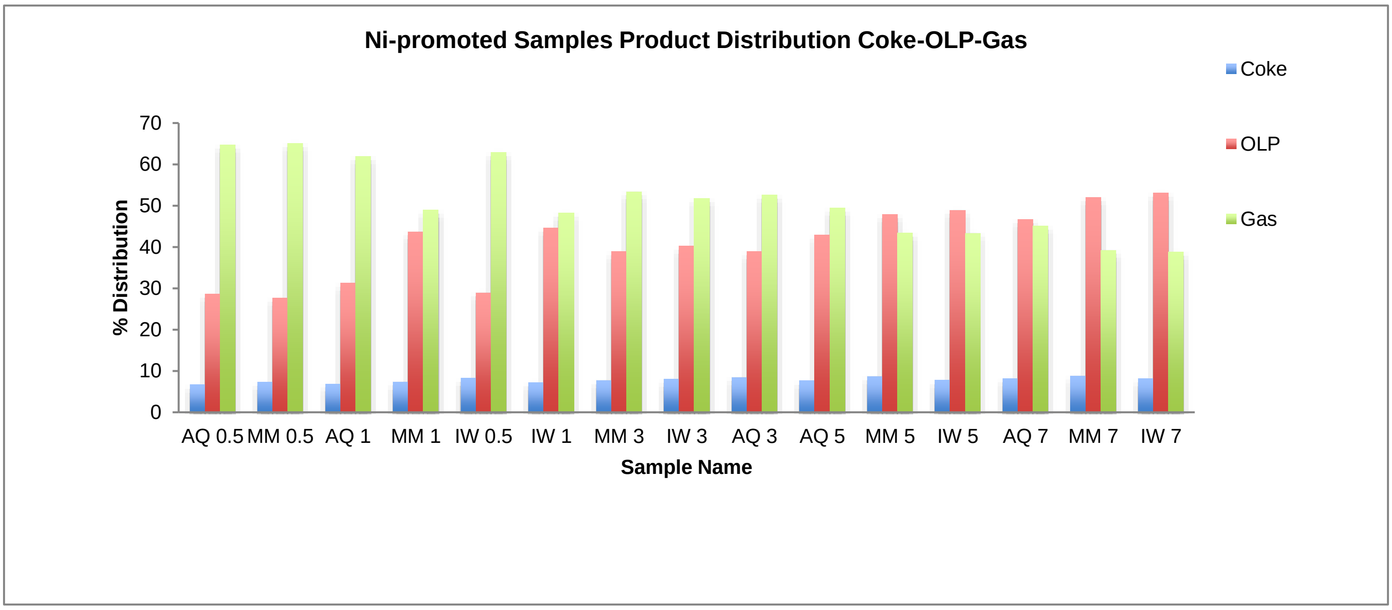


Figure 14, Coke, OLP and Gas product distribution of the Ni-promoted samples at 450℃, WHSV of 10.6 hr^{-1}

From *Figure 15*, the OLP distribution shows a non-linear decreases with increasing Ni-promotion from a minimum of 28.6% to a maximum of 46.7%, and minimum of 28.9% to a maximum of 53.1% for the AQ 0.5 - AQ 7 and IW 0.5 – IW 7 samples respectively. An overall increase was also observed for the MM 0.5 – MM 7 samples except that there was a trough observed at MM 3, 38.9% OLP. The minimum of 28.6% and a maximum of 52.0% were observed. The coke formation was on an overall increase as the Ni-promotion increased without exceeding 1.0000% ranging from 6.6670 to 8.8148%.

The decrease in OLP for both Ni may be attributed to the argument that promotion allows that cation to sit in the voids of the molecular sieve (HZSM-5) making it narrow and hence allowing only a molecules smaller than a threshold size.

4.3.4 The Effect of Ni-Loading on product distribution

The product distribution of the OLP was studied using the GC-MS chromatograms. The results suggest that the thermo-catalytic treatment of the feed produces mainly C_6-C_{12} hydrocarbons. In terms of product fractions by carbon chains, no significant changes were observed with increased Ni-loading. It is however notable that the changes in product distribution were more on the chemical structures of the components and OLP-Gas fractions as outline earlier. This study puts additional focus on the OLP based on the fact that the liquid fuels play a vital roles in the transportation sector. From the obtained results, in all cases, the highest mass fraction of the OLP was made up of C_8 compounds as suggested by the GC-MS chromatographs. Figures 15 – 17 show the product distribution by carbon chain length.

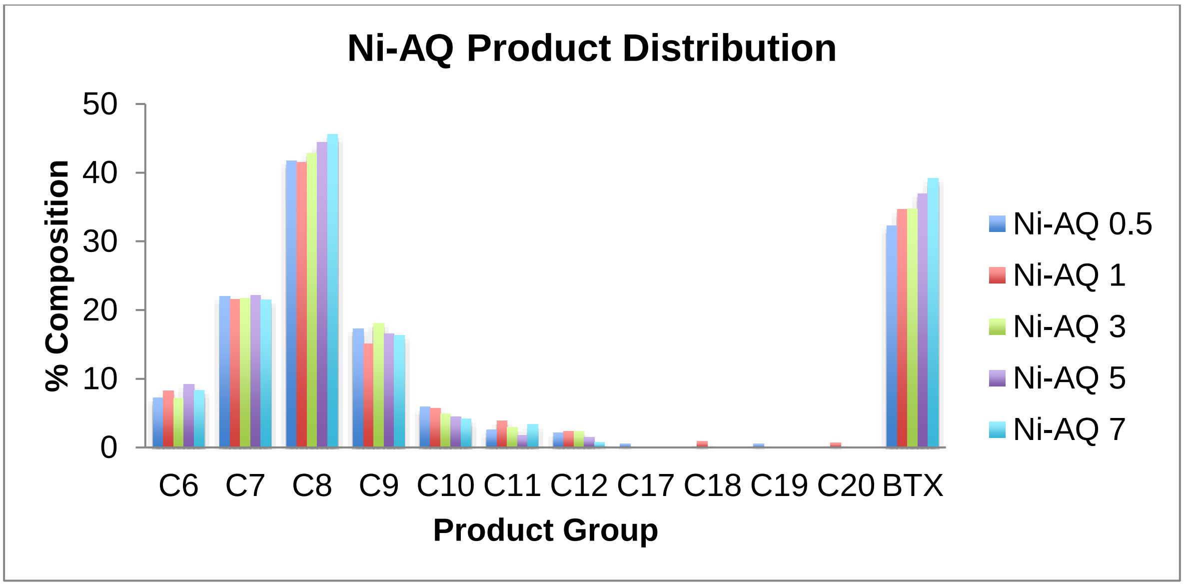


Figure 15, Product distribution by carbon chain length for Ni-AQ samples at 450℃, WHSV 10.6 hr^{-1}

From *Figure 15*, an increase in the % distribution of BTX with Ni-loading for the AQ samples was observed. Similar to the BTX product group, the C_8 fraction also increases with increasing AQ Ni-loading. This suggests that the increasing the AQ Ni-loading enhances the production of xylene as observed in *Figure 19,* where the only 14.1% of the detected C_8 components were non-xylenes. Essentially, the selectivity of xylene has influenced the increase of the C_8 mass fraction as the loading of Ni was increased.

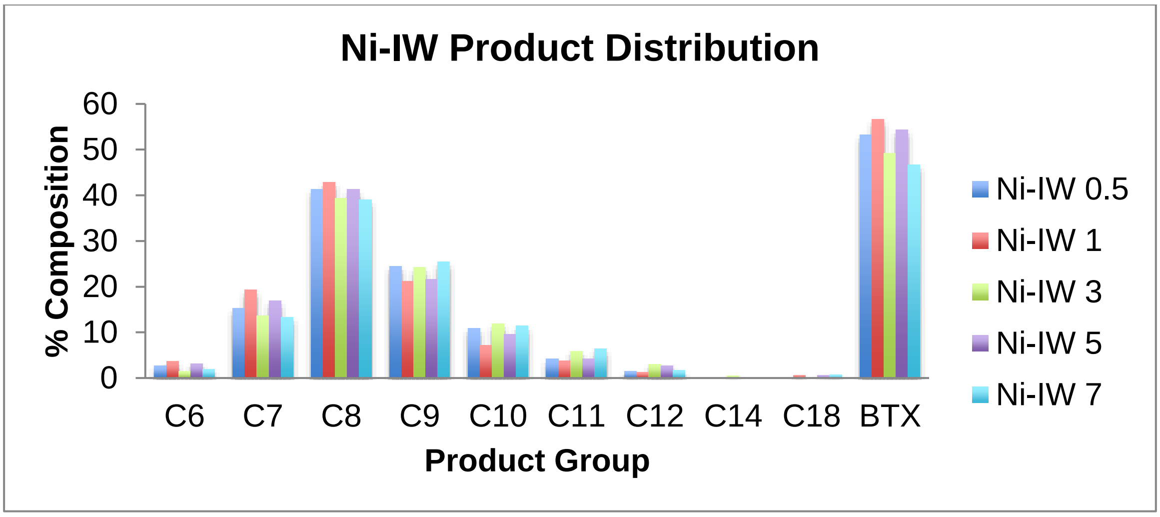


Figure 16, Product distribution by carbon chain length for Ni-IW samples at 450℃, WHSV 10.6 hr^{-1}

For IW samples the product fractions have a low mean deviation, less than 5.0000%, this suggests that the loading has little to no effect on the product group. It is however vital to note the consistency of the C_8 as the major fraction of the products. A conclusion may be drawn that these zeolite samples are selective towards C_8 hydrocarbons production. The BTX show a linear decrease in the Ni-IW 0.5, 3, and 7 (53.26 – 46.9% distribution) for this sample order with outliers (maxima) for the Ni-IW 1, 5 outliers reporting 56.65 and 54.39% respectively.

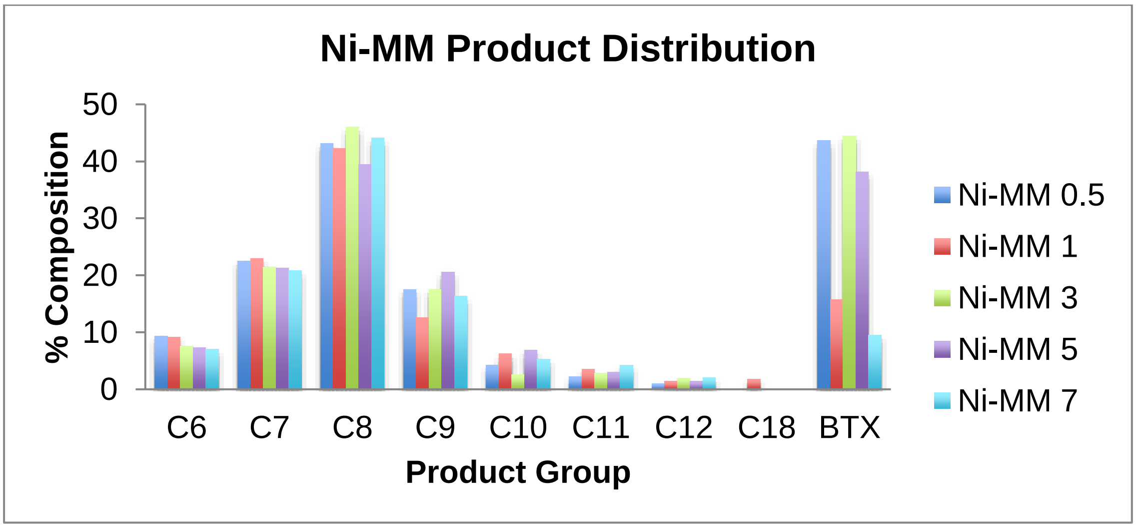


Figure 17, Product distribution by carbon chain length for Ni-MM samples at 450℃, WHSV 10.6 hr^{-1}

From the Figures 15 – 17, above, minor differences such as the order of increasing/ decreasing compositions of products groups and % of fractions within ± 5% were observed. The other difference was the increase of the distribution of the BTX compounds with increased Ni cation loading especially for the Ni-AQ samples. The similarities, however suggest that there was repeatability in the results in terms of classification by carbon chain lengths. The samples of promoted Ni-HZSM-5 displayed consistent products with chemical properties such as C_8 hydrocarbons dominating in the average range of 40 – 43.21%. The main carbon chain range of C_{6-12} (gasoline range) observed.

For all Ni-loaded samples, three major products that made up to more than 60% of the OLP distribution were classified as Xylenes, Cyclopentane Derivatives and Alkynes. The products fall in the carbon chain length of C_{7-8}. The alkynes were 1,3-Hexadien-5-yne and 1,5-Hexadien-3-yne while the main cyclopentane derivative observed was 1-ethenyl-3-methylene cyclopentene. The structures of these products are shown in *Figure 18* below:

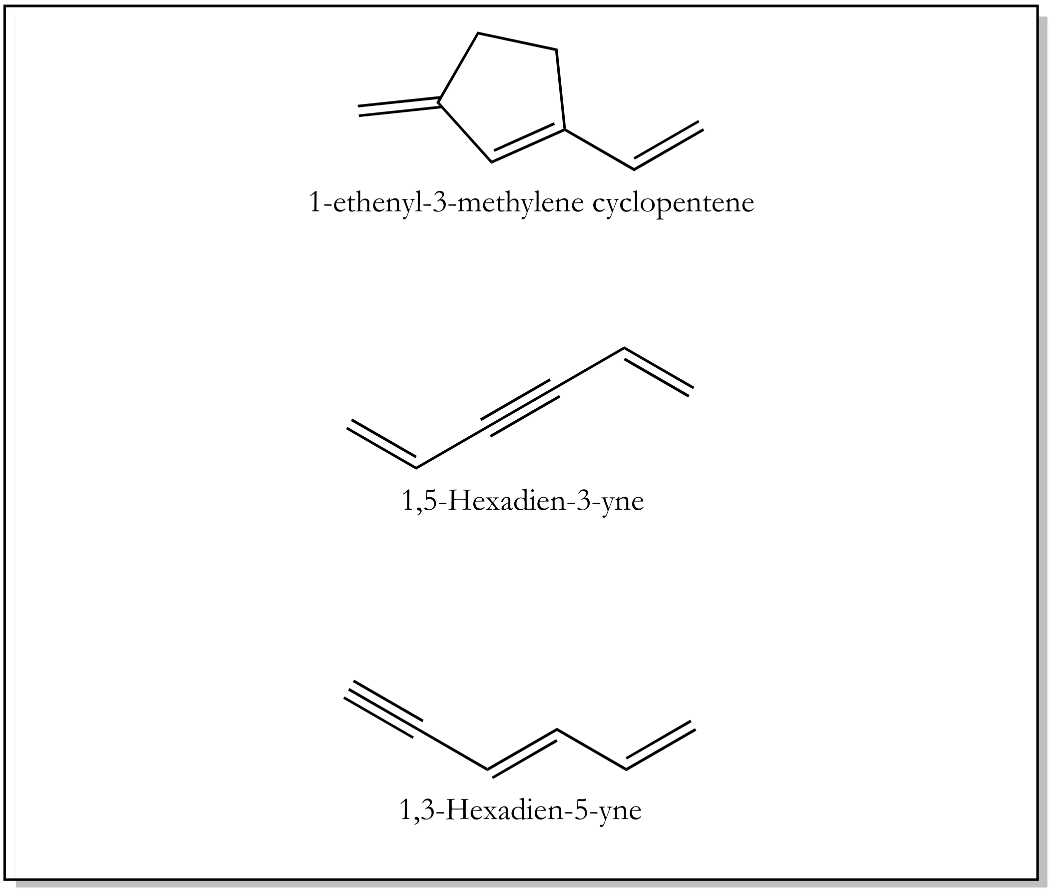


Figure 18, Chemical structures of the major products of the Ni-promoted samples at 450℃, WHSV 10.6 hr^{-1}

The effect of Ni-loading on HZSM-5 was an increase in the production of Xylenes, Cyclopentane Derivatives and Alkynes (XCA) as the loading was increased. Figures 19 – 21 below show the effect of Ni-loading on the distribution of (XCA).

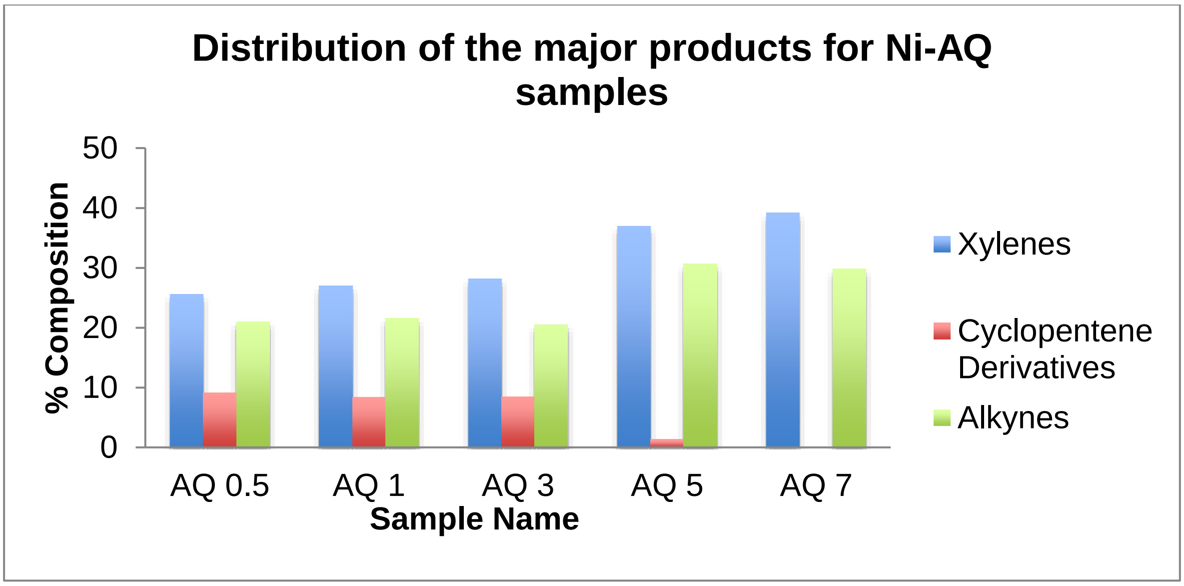


Figure 19, Xylenes, Cyclopentane Derivatives and Alkynes Distribution for Ni-AQ samples at 450℃, WHSV 10.6 hr^{-1}

From *Figure 19*, the % distribution of xylene increases with increasing Ni-loading from 25.62 – 39.16%. The alkynes gradually increase with the highest distribution at 30.65% Ni-AQ5 and a minimum of 20.5%.

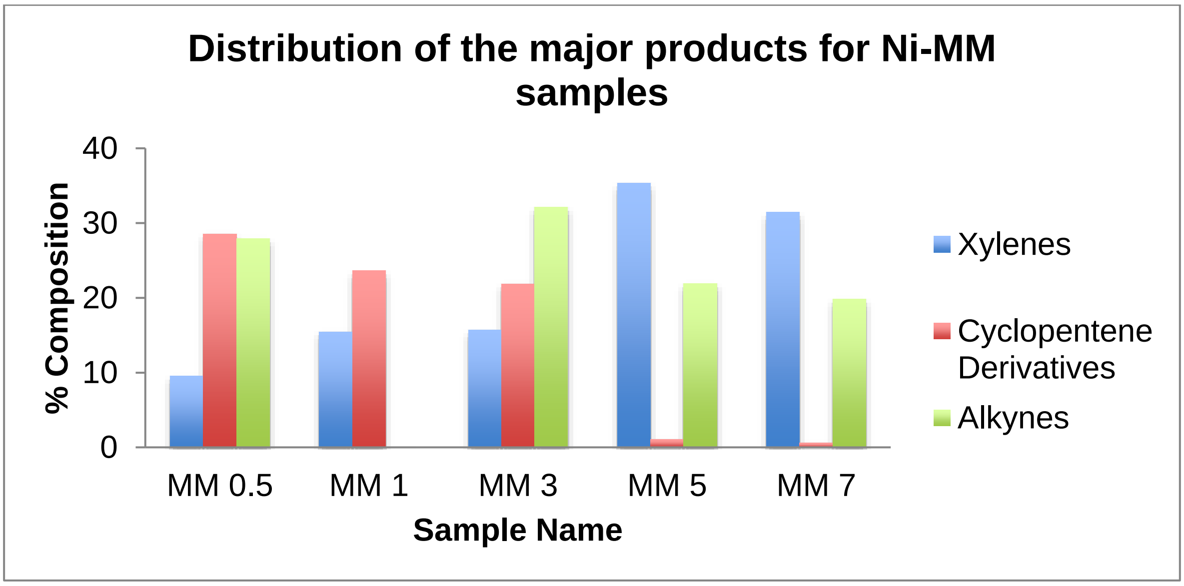


Figure 20, Xylenes, Cyclopentane Derivatives and Alkynes Distribution for Ni-MM samples at 450℃, WHSV 10.6 hr^{-1}

The % distribution of cyclopentane derivatives diminishes as the Ni-loading increases. This suggests that the product distribution of XCA was enhanced by the increased Ni-loading to an extent were the maximum combined selectivity of 69.76% XCA was achieved for the MM3 Nickel sample at 1.28% Ni.

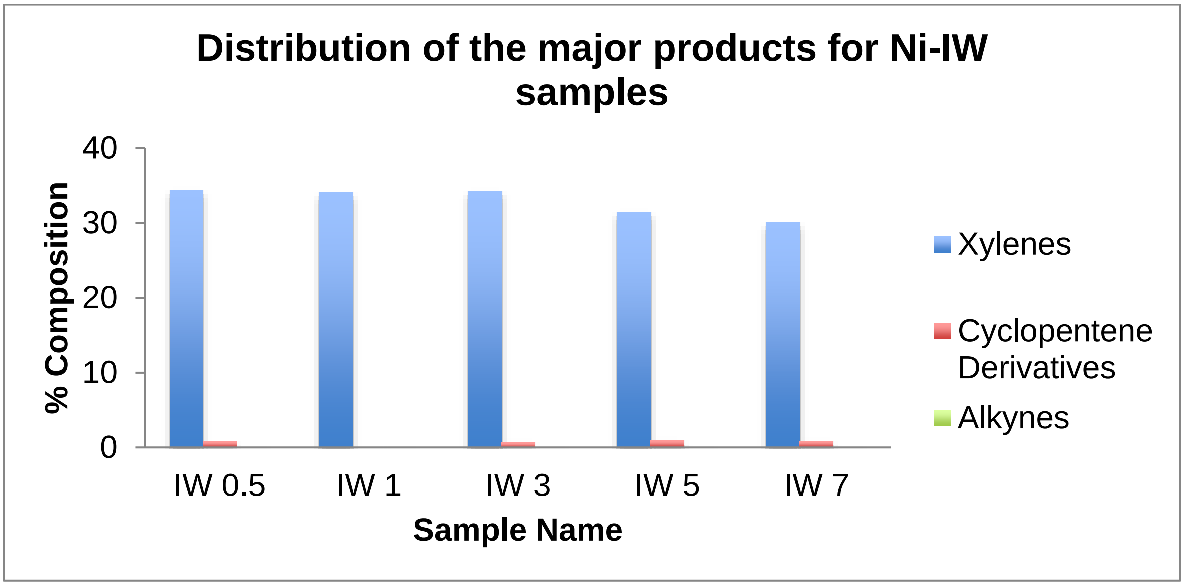


Figure 21, Xylenes, Cyclopentane Derivatives and Alkynes Distribution for Ni-IW samples at 450℃, WHSV 10.6 hr^{-1}

The loading of Ni using incipient wetness promotion shows how the promoter enhances the selectivity of Xylenes ranging from 30.12 – 34.32%. Cyclopentane Derivatives drastically decrease to detected amounts in the range of 0.62% to 0.92%. For IW promotion it is concluded that the loading % did not have a significant effect on the production of the XCA products in comparison to MM and AQ promotion but rather, the increased the selectivity of Xylenes form 4.05% to a maximum of 34.32% at 0.19% Ni as compared to the unpromoted HZSM-5 as shown by *Table 9*. While noting that Xylene is a member of the BTX products group, the results in *Figure 21*, explain the observation of maxima values (56.65 and 54.39%) BTX in *Figure 16*, as Xylene has substantial replaced the Alkynes.

4.3.5 The Effect of Sn-Loading on product distribution

Figures 22 – 24 show the distribution of carbon chain fractions ($C_{6\text{-}12}$) and for Sn-loaded samples.

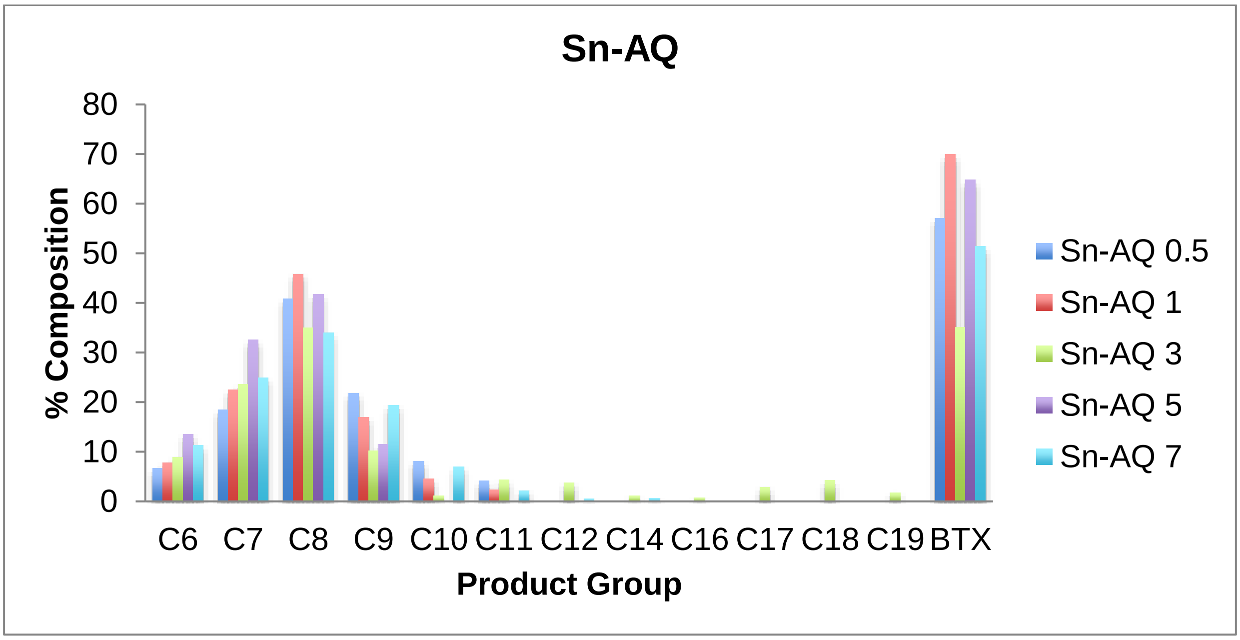


Figure 22, Product distribution by carbon chain length for Sn-AQ samples at 450°C, WHSV 10.6 hr^{-1}

From *Figure 22*, the results show that the distribution of the $C_{6\text{-}7}$ increase with the loading of the Sn-cation from the loading of 0.1 – 1.63% (loading range). C_6 fraction increased from 7.82 – 13.52% composition and 18.46 – 32.58% composition for C_7 fraction. The optimum maximum % compositions are at the Sn 1.63% for both C_6 and C_7 fractions. The further increase in Sn-loading up to 3.13% observed a decrease in the % distribution of 11.27 and 24.93% for C_6 and $_7$ respectively. The opposite (gradual decrease of % distribution with increased loading) was observed for the heavier fractions ($C_{8\text{-}12}$) within the same Sn-loading.

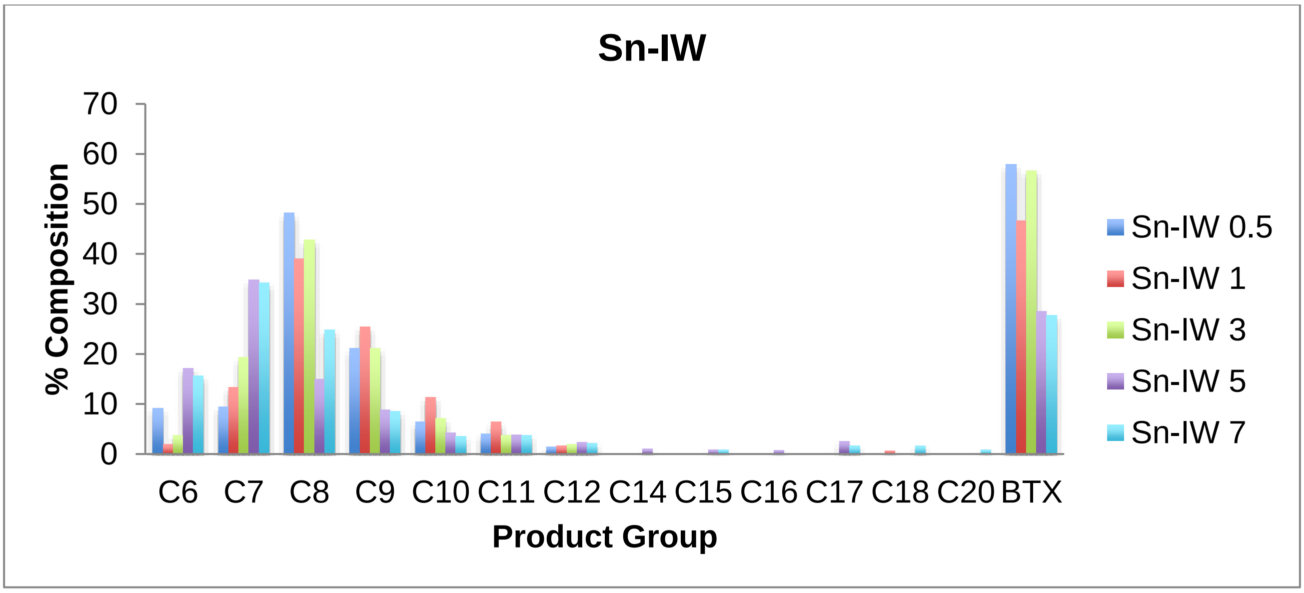


Figure 23, Product distribution by carbon chain length for Sn-IW samples at 450℃, WHSV 10.6 hr^{-1}

Figure 23 shows that the distribution of the C_7 increases with the loading of the Sn-cation from the loading of 0.31 – 2.99%. C_6 fraction increased from 7.82 – 13.52% composition and 18.46 – 32.58% composition for C_7 fraction. The optimum maximum % compositions are at the Sn 1.63% for both C_6 and $_7$ fractions. The further increase in Sn-loading up to 3.13% observed a decrease in the % distribution of 11.27 and 24.93% for C_6 and $_7$ respectively. The opposite (gradual decrease of % distribution with increased loading) was observed for the heavier fractions ($C_{8\text{-}12}$) within the same Sn-loading.

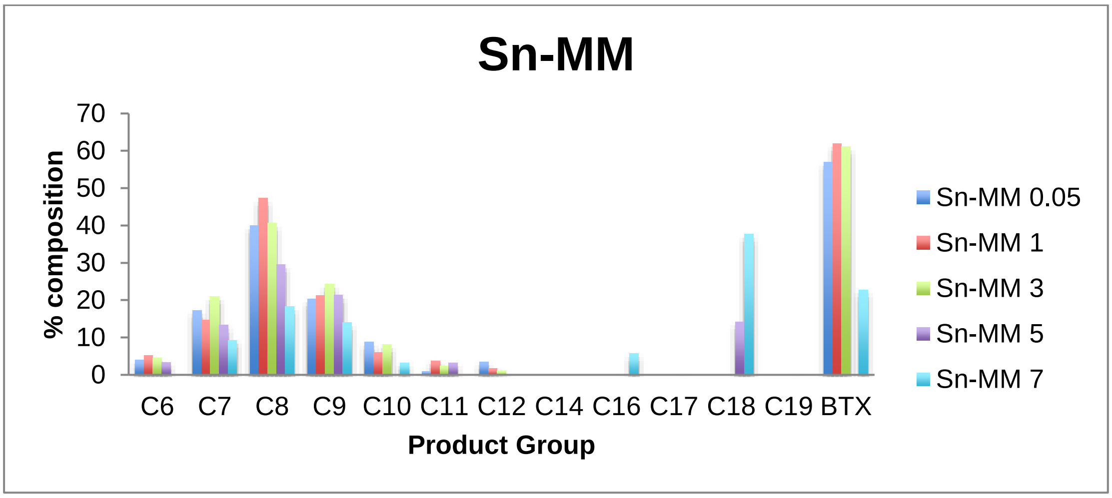


Figure 24, Product distribution by carbon chain length for Sn-MM samples at 450℃, WHSV 10.6 hr^{-1}

From the products obtained for the Sn-Loaded samples, it can be generalized that Sn is an aromatics promoter when supported on HZSM-5. These aromatics products are in agreement with the findings of Veses *et al.,* (2016) work that outline that Sn-promoted HZSM-5 produces aromatics through decarbonylation, de-oxygenation and aromatization reactions. For the increased loading of Sn by IW and AQ, the fractions of C_{6-8} increased gradually. This can be aligned with the idea that the degree of homogeneity achieved by promoting HZSM-5 by dissolving the $SnCl_2$ in water is higher than the homogeneity achieved by mechanical mixing. In all the three cases (IW, AQ and MM) the results show that the increase in the C_8 aromatics as gradual but this was only true at lower loading range (0.25 – 1.77%) for MM. In the same loading range the fractional conversion of the feed was ≈100%. At higher loading range (2.73 – 3.82%) the fractional conversion was low as shown in

Table 11, this presents why the aromatic fraction was lower, in agreement with material balance.

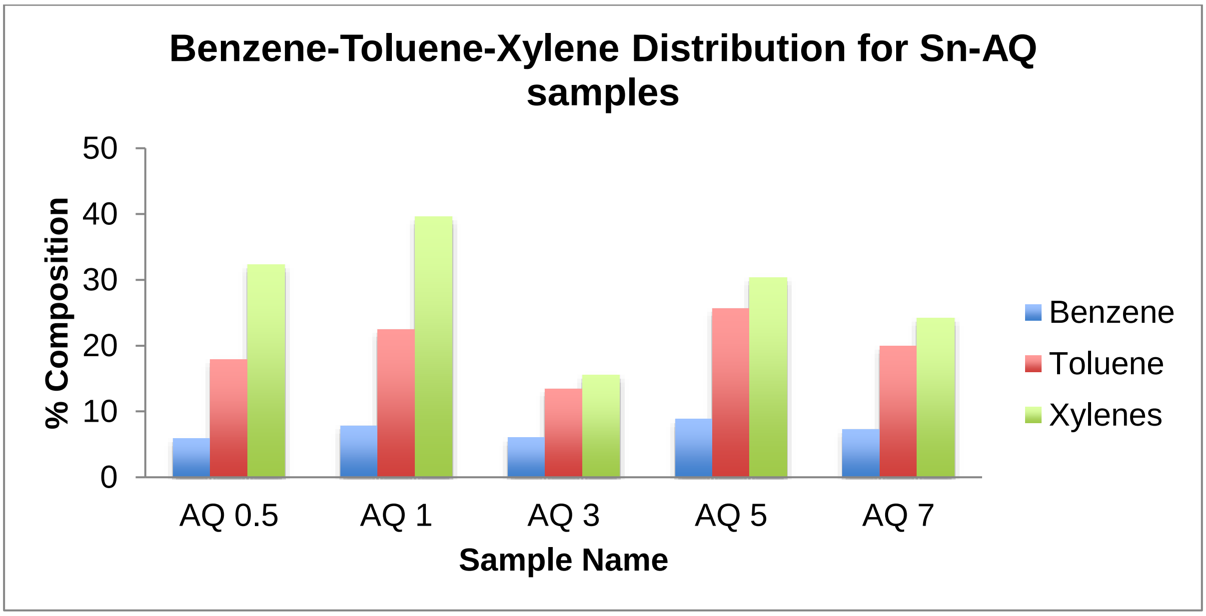


Figure 25, Benzene-Toluene-Xylene Product distribution for Sn-AQ samples at 450℃, WHSV 10.6 hr^{-1}

The selectivity of Xylenes increases from 32.29 – 39.61% when the Sn-loading was increased from 0.10 - 0.36%. With Xylene being a benzene derivative, the decline in the selectivity of Xylene with further loading with a minimum selectivity at 0.9% Sn concentration may be attributed to a possibility of the zeolite pores being reduced as the promoter cation of Sn occupies the sites in the pores of the HZSM-5 in turn inhibiting the shape and size of the Xylene molecules. Adjaye, Katikaneni and Bakhshi, (1996) confirmed the role of zeolite pore size in the product selectivity. They however further indicated that thermal cracking of long chains to shorter ones is also an essential step in product selectivity. In this study, the temperature of the reactor was kept constant at ±450 °C. on the basis of constant temperature; it is assumed that the thermal cracking was fairly constant at least in terms of the initial reaction. Thus, the effect observed is assumed to be caused by the size of the pores accessed by the shorter carbon chains before they react further to form the detected products.

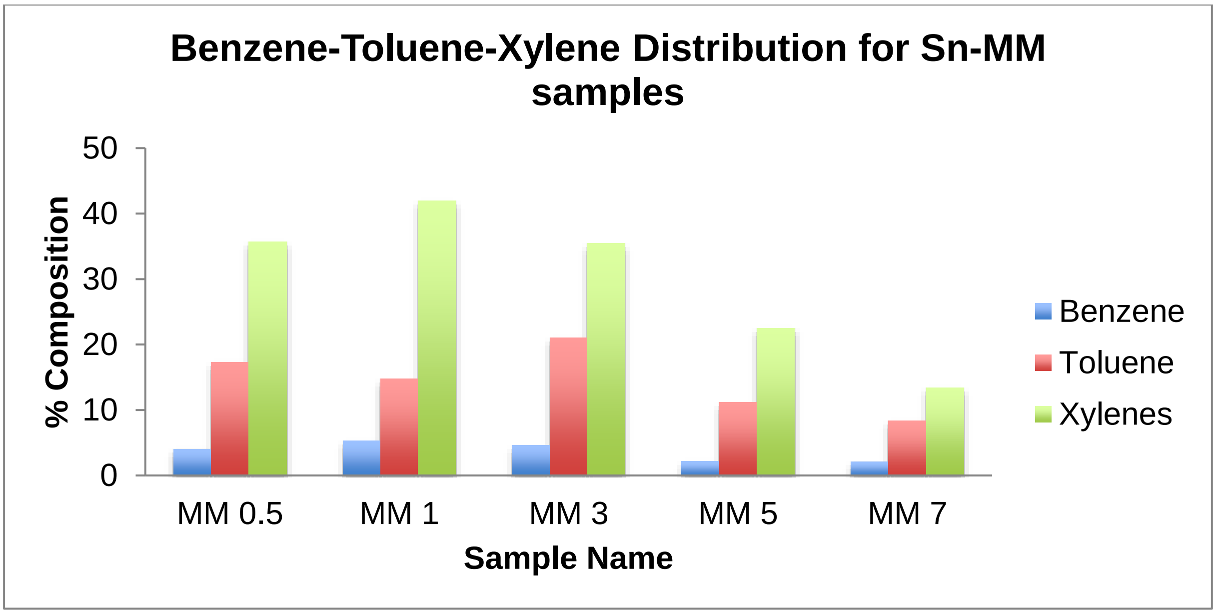


Figure 26, Benzene-Toluene-Xylene Product distribution for Sn-MM samples at 450℃, WHSV 10.6 hr^{-1}

All the Sn-MM samples produced BTX products in a B>T>X fashion. However, the MM1 sample produced the maximum Xylene at 41.97%, as the loading increased, the amount of Xylene declined gradually, reaching a minimum value of 13.36% for sample MM7. A similar trend was observed for Benzene (maximum of 5.27 and a minimum of 2.12%) but not Toluene. The amount of Toluene was maximum at 21.01% for sample MM3 and minimum at 8.35% for sample MM7.

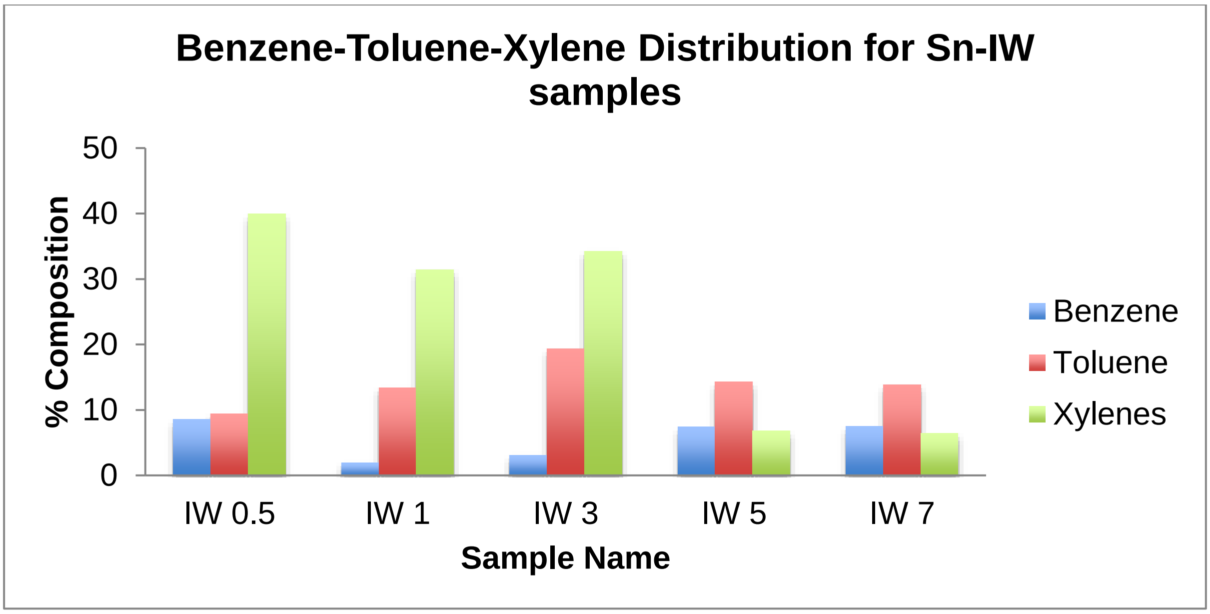


Figure 27, Benzene-Toluene-Xylene Product distribution for Sn-IW samples at 450℃, WHSV 10.6 hr^{-1}

IW samples produced a BTX, the amount of these products fluctuated by alternating between a maximum of 57.94% at IW 0.5 and a minimum of 27.77% at IW 7.

The Sn promoted samples were selective towards aromatics. It is worth examining the aromatic content of different streams to identify quantitative product distribution due to the effect of Sn loading.

Table 12, Table showing the percentage of Aromatics in the liquid product streams as a percentage of feed

Sample ID	**0.5**	**1**	**3**	**5**	**7**
	Aromatics (%)	**Aromatics (%)**	**Aromatics (%)**	**Aromatics (%)**	**Aromatics (%)**
Ni-AQ	19.2	20.8	27.3	30.0	31.8
Sn-AQ	32.1	33.8	13.3	43.6	43.3
Ni-IW	28.5	43.9	45.6	47.3	53.1
Sn-IW	51.7	50.5	50.2	33.3	44.5
Ni-MM	20.8	33.9	16.8	36.6	23.0
Sn-MM	29.6	52.00	27.8	11.7	11.0

The aromatic content in a product stream was calculated by finding the mass of aromatic product components in the OLP using the sum of the individual mass fractions of aromatics. Analysing the aromatic content of the OLP product streams gives a better understand of the fraction of the feed that converted to aromatics in the different product streams at different loading. From *Table 12,* the aromatic % for Sn loaded samples equate closely to the OLP values in *Figure 13*, showing that the OLP of Sn samples was almost purely aromatic with an exception of the low conversion streams of the samples; MM 5 and 7 that have relatively low aromatics as described in section 4.3.2. The same (purely aromatic streams) was observed for the Ni-IW samples, in agreement with the observation in *Figure 21,* that suggest a higher product distribution of Xylene (aromatic) as opposed to the Alkynes.

4.3.6 The effect of promoters on conversion products and their applications

The results suggest that the products that emanate from the reactor depend on the promoter; i.e. Ni promotes the production of compounds different from Sn. Having pointed that out, it should however be noted that the overlap in the identity of compounds produced by both Ni and Sn is not ignored. The catalyst system is HZSM-5 based in both cases, hence, similarities in products cannot be completely ruled out. This work lists the observed differences in the products as suggested by the Ni/Sn promoters.

4.3.7 Aromatics

Several aromatics were found in the product streams, predominantly in the Sn-loaded sample's products. Some of the more common aromatics that were found in most of the product streams are shown in *Table 13.* Aromatics have a high octane number, which is usually above 100. Octane number (ON) is the ability of a fuel to resist spontaneous combustion when compressed which will result in a knocking effect in the engine. N-Octane has is assigned a 100 for octane rating and n-heptane is assigned a zero (0) on the octane rating. Therefore adding aromatics to a petrol blend will result in an improvement in the octane rating of the fuel, which thereby improves the performance of the fuel. *Table 13* also shows the associated ON of the aromatics in the product streams.

Table 13. Octane number (ON) for aromatic compounds

Compound	Octane Number (ON)
Benzene	114.8
Toluene	120.1
Ethyl-benzene	107.4
m-Xylene	145.0
o-Xylene	120.0
p-Xylene	146.0

Naphthalene, commonly called mothballs, is used for storing clothes and other material that can be damaged by moulds or moth larvae. Prior to World War 2, it was also used to increase the ON of petrol. However, because of mothballs are more expensive than petrol it is no longer economical to add naphthalene to petrol. Other used of naphthalene include the manufacturing of plastics, resins, fuels, and dyes. Benzene is usually a limited additive in petrol because of its carcinogenic nature even though it has a high ON. Therefore, the common uses of benzene include making plastics, synthetic fibres, rubber lubricants, dyes, resins, detergents and drugs. Derivatives of benzene such as toluene and xylene are the ones usually added to petrol to increase the ON number and they usually comprise up to 25% of petrol. Other aromatic compounds found in the products stream such as indane can be fed into a catalytic converter to produce xylene. Toluene is used to produce rubber, paints, glues, adhesives and as a thinning agent because it helps dry and dissolve other substances. In addition, it is also used in the cosmetics industry as a nail polish remover.

4.3.8 Straight and Branched – Chains

The Ni-loaded samples produced several straight and branched chained alkanes, alkenes, and cyclic products were found in the product streams. A few examples of those products and their respective uses will be mentioned. 1-Octene is a linear organic compound that is mostly used as an intermediate in the production of polyethene raisins to produce high-density polyethene (HDPE) and low density polyethene (LDPE). Its isomer Cyclooctene undergoes ting open metathesis polymerization to give polyoctenamers, which are marketed under the name Vestenamer. Several other uses of 1-octene include being a surfactant, as a lubricant, as a synthetic acid and in the pulp and paper industry.

Heptane is another compound that is normally found in petrol, though in small amounts because it is the zero-rating of the ON because it spontaneously ignites when compressed a little. Therefore, most gasoline fuels have a maximum of 13% heptane to enable a higher-octane number to be achieved. Additional uses of heptane include being used for anaesthetics, cements, compounders, inks, lab reagents, organic synthesis and solvents. It is also found in laboratories and it is used as a solvent. Octane, which has a 100 rating on the ON scale, was one of the compounds found in the product stream. For a petroleum blend, the higher the ON the more compression the fuel can withstand before detonating. Therefore, blends with higher ONs find application in high performance petrol engines, which require higher compression ratios.

Cyclohexene is an unsaturated carbon, which is a volatile liquid under room conditions, and find application in diverse chemical reactions because of the reactivity of the unsaturated double bond. It also has industrial and consumer uses in the following that include the synthesis of waterproof coatings, LED encapsulation systems, crack resistant films, tie binder for coating, adhesives, silanes and it is also a precursor to the epoxide, diol and other useful downstream products. Another compound found in the product stream was nonane. It is a colourless, flammable liquid, occurring primarily in the kerosene fractions of the distillation column. Kerosene’s major application is as a fuel in aeroplanes (jet-fuel) and tractors and for home heating purposes. Several other uses of nonane include being an organic solvent, reaction intermediate in in the perfume industry, in rose, lily, and peony, as a distillation chaser, as a fuel additive, a component in biodegradable detergents and in solid separation processes.

4.3.9 The effect of promotion technique on catalytic activity

No single measurement sufficiently solely represents catalytic activity; however, the purpose of the catalyst in this work is to achieve desired products during the conversion of the feed. Multiple measures including the selectivity of desired products and lower percentage distribution of the undesired products present a measure of an active catalyst that produces the desirable results. To present the effect of promotion techniques on catalytic activity, the products that emanate from the reactor and their value is evaluated to qualify activity.

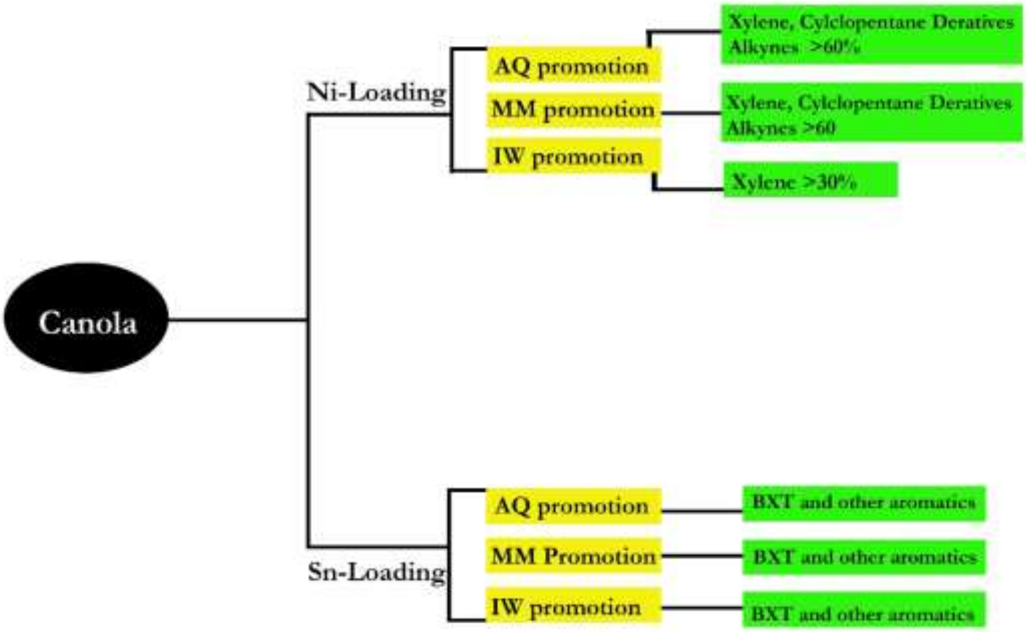


Figure 28, A representation on catalytic activity of the Ni and Sn loaded samples based on conversion products

From *Figure 28*, shows the activity of the Ni and Sn loaded samples. Increase in the production of various products such as Xylene, Cyclopentane derivatives and Alkynes was observed for Ni-loaded samples. The unpromoted commercial HZSM-5 catalyst did produced 7.18% Xylenes and no Cyclopentane Deravatives and Alkynes were detected. This suggests that Ni-loading exhibited increased catalytic activity towards XCA production for samples loaded using AQ and MM techniques. The samples loaded by IW technique showed activity towards producing Xylene but not Cyclopentane Derivatives or Alkynes. It may be concluded that the atomic radius of the Ni cation increased the selectivity of the sample for the XCA products. Botas *et al.,* (2014), studied the products of Ni-modified HZM-5 and established that the introduction of Ni has increased the production of unsaturated hydrocarbons lighter than the C_{18} hydrocarbons. The other metals with higher atomic radii were found to be more selective towards the aromatics. In agreement with their work, the results obtained from this study show the uplifted selectivity toward BTX and aromatics when HZSM-5 was promoted with Sn. Other researchers; Veses *et al.,* (2015) also presented BTX, substituted benzenes in the gasoline range to be the major products of Sn-loaded HZSM-5. Furthermore, their study also reported that Sn-loaded HZSM-5 produces a wide spectrum of benzene derivatives.

CHAPTER 5

Conclusion and Recommendation

In this work, the effect of metal loading on the HZSM-5 samples was studied on various parameters, namely: fractional conversion. In order to establish the effect metal loading on the fractional conversion, an unpromoted HZSM-5 was tested in the reactor and the liquid product was analysed for the presence of the components that were initially in the feed. It was established that for HZSM (unpromoted) at a 450°C and a WHSV 10.6 hr^{-1}, the conversion was ~100% within the GC-MS detection limits. Similarly, for all the samples promoted with Ni, no original components were detected. This led to the conclusion that there is no effect of Ni-loading on the fractional conversion with the specified reaction conditions.

In a similar fashion, the results obtained for Sn-loaded samples was also studied, MM 5 and MM 7 samples were the only samples in who's products the carboxylic acids were detected. Based on this observation, it was concluded that the loading of Sn on HZSM-5 by mechanical mixing has an effect on conversion, reducing fractional conversion from ~100% to a minimum of 77.9 for MM 7. The MM 5 sample reported a conversion of 91.4%. From these figures, it was concluded that the fractional conversion of canola over Sn-loaded HZSM-5 diminishes at higher loading percentage.

The product distribution was studied as fractions (Gas, OLP and Coke) and also the % composition of groups of products classified according to chain length, family/ class of compounds i.e. aromatics, BTX, XCA and so on in the OLP using GC-MS. The gas composition was studied using GC-TCD. To achieve the objective of studying the effect of metal loading on the product distribution, the identity and composition of the product streams were compared to those of the unpromoted HZSM-5 while varying the metal type (Ni or Sn) and the loading percentage as shown in *Figure 10* and *Figure 11*. It was then assumed that the difference in the product distribution was due to metal loading. It was concluded that the metal loading had minimal effect on the product distribution as no major changes were observed for the Ni and Sn loading. It was however established that the HZSM-5 converted the feed to CO, of 5.2834 ± 0.3742%

CO_2 of 15.1612 ± 0.2742% and CH_4 10.2008 ± 0.5421%. These relatively low standard deviations in the gas product distributions led to a conclusion that the loading had minimal effect on gas product quality.

This study concludes that in terms of selectivity, the Ni loaded samples were the most selective and robust in targeting XCA and minimizing heavier molecular weight compounds (C_{12-18}) in the products. This may in turn be recognized as a gasoline range chemicals promoter. While it is notable that Sn loaded samples also produced gasoline range hydrocarbons, the short coming with Sn was that the products where almost entirely benzene derivatives and no olefins. The relationship between promotion techniques and catalytic activity was studied by comparing the quality and identity of products obtained at the same target loading for the three different techniques. The promotion efficiencies suggest that the different techniques impose different efficiencies based state i.e. when in solution, the loading is more efficient than in solid state as the cations are not as mobile. The deposition of cations by different techniques may also cause different properties on the promoted samples.

To better understand the directing properties of the HZSM-5 based samples and promoters, it is recommended that a surface properties study including surface area, pore size and crystallinity of the samples be compared with that of the unpromoted HZSM-5 to predict the catalytic properties. Other chemical properties including acidity may also add value in terms of better understanding the activity of metal promoted HZSM-5.

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Appendices

Sample Calculations

% Loading of Cations Calculations

Molecular weight of $NiCl_2.6H_2O$ = 237.69g/mol

Molecular weight of $SnCl_2$ = 189.60g/mol

If X_{cation} is the mass fraction of the loaded cation on the virgin commercial HZSM-5 per mole of salt used, then, X_{cation} may be denoted as either X_{Nickel} or X_{Tin}. Using the equation:

$X_{cation} = M_{cation} \div (M_{cation} + M_{HZSM\text{-}5})$

where M_{cation} = Mass of the cation and $M_{HZSM\text{-}5}$ = Mass of HZSM-5

X_{Nickel} = 58.69g/mol ÷ 237.69g/mol = 0.2469

X_{Tin} = 118.71gm/mol ÷ 189.60g/mol = 0.62611

The equation can then be solved for M_{cation} , since X and $M_{HZSM\text{-}5}$ are known in all cases

Fractional Conversion

Using sample Sn-MM 5 the fractional conversion sum of all the components in the feed = 16.53%. To obtain the % of the feed that converted in; %OLP x sum of unreacted components. 100 – uncoverted componetnts in OLP fraction = % of the feed that did not react. Fractonal conversion = 100 – the fraction that did not react.

% conversion of feed = 100% - (16.53% x 0.52) = 91.40%

Aromatic content as % of feed

Using sample Sn-MM 1 the aromatic % in the OLP is the sum of all the aromatics = 100%. To obtain the % of the feed that converted to aromatics, the % OLP x % aromatics in OLP as a fraction = Aromatics content as % of the feed.

Aromatic content as % of feed = 52.00% x 100/100 = 52.00%

A1: XRF Metal concentration and product material balances

Nickel Promoted Samples		Tin Promoted Samples		Ni-OLP (%)	Sn-OLP (%)	Ni Aromatic (%)	Sn Aromatic (%)	Ni (%)	Sn (%)	Ni-Coke/ g/100 g feed	Sn-Coke/g/ 100g feed
	XRF Ni (%)		XRF Sn (%)			GC-MS	GC-MS	GAS	GAS		
AQ 0.5	0,10	**AQ 0.5**	0,10	28,60	32,50	19,20	32,10	64,73	60,48	6,6670	7,0154
MM 0.5	0,14	**MM 0.5**	0,25	27,70	29,60	20,80	29,20	65,05	63,29	7,2536	7,1142
AQ 1	0,16	**IW 0.5**	0,31	31,30	33,80	20,80	51,70	61,92	59,06	6,7821	7,1366
MM 1	0,18	**AQ 1**	0,36	43,70	30,70	33,90	33,80	48,97	61,59	7,3310	7,7142
IW 0.5	0,19	**MM 1**	0,43	28,90	52,00	28,50	30,70	62,84	39,31	8,2561	8,6876
IW 1	0,41	**IW 1**	0,54	44,60	51,80	43,90	50,50	48,25	40,67	7,1532	7,5271
MM 3	1,24	**AQ 3**	0,95	38,90	25,30	16,80	13,30	53,38	66,58	7,7213	8,1249
IW 3	1,28	**AQ 5**	1,63	40,20	51,90	3,70	43,60	51,80	39,68	7,9987	8,4168
AQ 3	1,33	**MM 3**	1,77	38,90	27,83	27,30	12,10	52,66	63,29	8,4387	8,8798
AQ 5	1,47	**IW 3**	1,86	42,90	52,69	30,00	50,20	49,44	39,25	7,6583	8,0586
MM 5	1,61	**MM 5**	2,73	47,90	47,90	36,60	39,60	43,44	42,98	8,6623	9,1150
IW 5	1,92	**IW 5**	2,99	48,90	30,70	47,30	11,70	43,33	61,12	7,7715	8,1777
AQ 7	2,14	**AQ 7**	3,13	46,70	50,60	31,80	43,30	45,14	40,82	8,1553	8,5815
MM 7	2,69	**MM 7**	3,82	52,00	52,00	23,00	44,50	39,19	38,72	8,8148	9,2755
IW 7	3,00	**IW 7**	4,27	53,10	29,60	53,10	11,00	38,78	61,85	8,1238	8,5484

A2: Product fractions by chain length for Ni-loaded samples

Ni Samples

Sample	C6	C7	C8	C9	C10	C11	C12	C17	C18	C19	C20	BTX
Ni-AQ 0.5	8,28	21,55	41,51	15,07	5,73	3,87	2,36		0,92		0,69	34,65
Ni-AQ 1	7,21	22,02	41,71	17,3	5,95	2,55	2,15	0,57		0,52		32,29
Ni-AQ 3	8,33	21,47	45,57	16,32	4,17	3,35	0,77					39,16
Ni-AQ 5	7,16	21,69	42,86	18,11	4,9	2,91	2,36					34,74
Ni-AQ 7	9,21	22,13	44,41	16,58	4,49	1,74	1,45					36,96

Sample	C6	C7	C8	C9	C10	C11	C12	C14	C8	BTX
Ni-IW 0.5	3,13	16,94	41,27	21,59	9,59	4,21	2,73		0,56	54,39
Ni-IW 1	1,91	13,35	39,07	25,44	11,39	6,46	1,68		0,68	46,69
Ni-IW 3	2,73	15,32	41,28	24,44	10,89	4,23	1,52			53,26
Ni-IW 5	3,72	19,35	42,81	21,2	7,16	3,8	1,32		0,65	56,65
Ni-IW 7	1,45	13,64	39,4	24,22	11,89	5,85	3,05	0,50		49,18

Sample	C6	C7	C8	C9	C10	C11	C12	C18	BTX
Ni-MM 0.5	9,38	22,48	43,15	17,52	4,26	2,24	0,97		43,67
Ni-MM 1	7,31	21,29	39,49	20,54	6,89	3,06	1,41		38,16
Ni-MM 3	7,05	20,86	44,11	16,37	5,32	4,24	2,04		9,52
Ni-MM 5	7,57	21,46	46,03	17,52	2,62	2,84	1,97		44,48
Ni-MM 7	9,17	22,99	42,26	12,57	6,27	3,55	1,40	1,80	15,71

A3: Product fractions by chain length for Sn-loaded samples

Sn Samples

Sample	C6	C7	C8	C9	C10	C11	C12	C14	C16	C17	C18	C19	BTX
Sn-AQ 0.5	6,66	18,46	40,84	21,83	8,09	4,13							57,06
Sn-AQ 1	7,82	22,49	45,81	16,95	4,55	2,36							69,92
Sn-AQ 3	8,9	23,62	34,96	10,2	1,12	4,33	3,74	1,11	0,76	2,89	4,30	1,75	35,06
Sn-AQ 5	13,52	32,58	41,78	11,48									64,82
Sn-AQ 7	11,27	24,93	33,99	19,4	6,99	2,19	0,56	0,65					51,40

Sample	C6	C7	C8	C9	C10	C11	C12	C14	C15	C16	C17	C18	C20	BTX
Sn-IW 0.5	9,18	9,41	48,21	21,19	6,42	4,08	1,49							57,94
Sn-IW 1	1,91	13,35	39,07	25,44	11,39	6,46	1,68					0,68		46,69
Sn-IW 3	3,72	19,35	42,81	21,2	7,16	3,8	1,97							56,65
Sn-IW 5	17,13	34,87	15	8,84	4,27	3,81	2,35	1,03	0,84	0,73	2,55			28,54
Sn-IW 7	15,68	34,24	24,82	8,58	3,56	3,72	2,19		0,88		1,67	1,65	0,87	27,77

Sample	C6	C7	C8	C9	C10	C11	C12	C14	C16	C17	C18	C19	BTX
Sn-MM 0.5	4.03	17.29	40.02	20.37	8.85	0.96	3.42						56.98
Sn-MM 1	5.27	14.74	47.36	21.21	5.97	3.77	1.68						61.98
Sn-MM 3	4.60	21.01	40.66	24.33	8.11	2.39	1.08						61.07
Sn-MM 5	3.32	13.34	29.57	21.36	5.42	3.16	0.97		2.33	0.88	14.20	0.53	35.76
Sn-MM 7	0.00	9.24	18.37	14.06	3.16	1,24			5.72		37.66		22.75

A4: XCA distribution for Ni-loaded Samples

	Xylenes (%)	Cyclopentane Derivatives (%)	Alkynes (%)
AQ 0.5	25.62	9.1	21.02
AQ 1	26.99	8.41	21.55
AQ 3	28.18	8.42	20.5
AQ 5	36.96	1.36	30.65
AQ 7	39.16	-	29.8

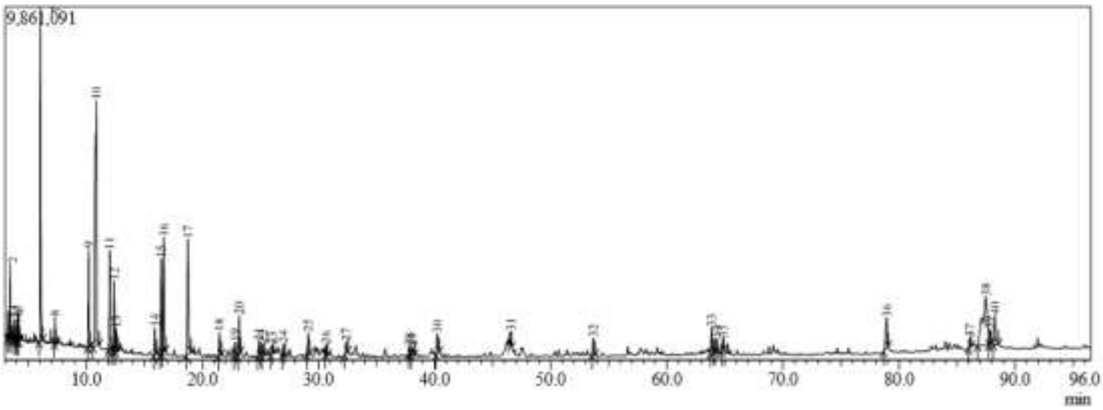
	Xylenes (%)	Cyclopentane Derivatives (%)	Alkynes (%)
MM 0.5	9.52	28.56	27.91
MM 1	15.45	23.63	-
MM 3	15.71	21.86	32.16
MM 5	35.37	1.08	21.89
MM 7	31.44	0.59	19.84

	Xylenes (%)	Cyclopentane Derivatives (%)	Alkynes (%)
IW 0.5	34.32	0.79	-
IW 1	34.09	-	-
IW 3	34.2	0.62	-
IW 5	31.43	0.92	-
IW 7	30.12	0.83	-

A5: BTX distribution for Sn-loaded Samples

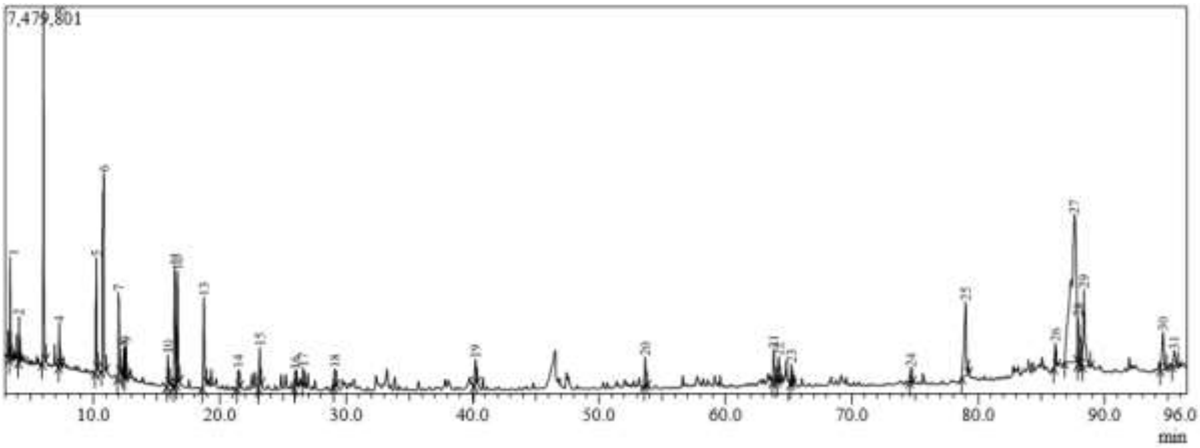
	Benzene (%)	**Toluene (%)**	**Xylenes (%)**
AQ 0.5	5.9	17.87	32.29
AQ 1	7.82	22.49	39.61
AQ 3	6.05	13.45	15.56
AQ 5	8.83	25.67	30.32
AQ 7	7.28	19.94	24.18
	Benzene (%)	**Toluene (%)**	**Xylenes (%)**
MM 0.5	4.03	17.29	35.66
MM 1	5.27	14.74	41.97
MM 3	4.6	21.01	35.46
MM 5	2.14	11.16	22.46
MM 7	2.12	8.35	13.36
	Benzene (%)	**Toluene (%)**	**Xylenes (%)**
IW 0.5	8.59	9.41	39.94
IW 1	1.91	13.35	31.43
IW 3	3.1	19.35	34.2
IW 5	7.44	14.28	6.82
IW 7	7.48	13.88	6.41

A6: Sn-MM 5 Chromatograph



Peak#	R.Time	Area%	Name
1	3.263	0.67	Cyclopentene, 1-methyl-
2	3.429	2.14	Benzene
3	3.747	0.51	Cyclohexene
4	3.939	0.56	1-Heptene
5	4.118	0.71	Hexane, 3-methyl-
6	4.187	0.91	1,3-Pentadiene, 2,3-dimethyl-
7	6.056	11.16	Toluene
8	7.310	0.97	Undecane, 2,4-dimethyl-
9	10.225	4.03	Ethylbenzene
10	10.853	17.70	p-Xylene
11	12.025	4.76	o-Xylene
12	12.416	3.08	Cyclooctene, (Z)-
13	12.589	0.89	Nonane
14	15.906	1.28	Benzene, propyl-
15	16.460	4.43	Benzene, 1-ethyl-2-methyl-
16	16.673	5.37	Benzene, 1-ethyl-2-methyl-
17	18.750	6.24	Benzene, 1,2,3-trimethyl-
18	21.467	1.30	Indane
19	22.813	0.74	Benzene, 1-methyl-3-propyl-
20	23.170	1.85	2-Tolyloxirane
21	24.870	0.73	Benzene, 1-ethenyl-3-ethyl-
22	25.226	0.70	Benzene, 2-ethyl-1,4-dimethyl-
23	25.989	0.49	1-Undecene
24	26.977	0.58	1-Undecanol
25	29.120	1.17	Benzene, 1-ethenyl-4-ethyl-
26	30.635	0.55	3-Phenyl-1-butanol
27	32.381	0.65	1H-Indene, 2,3-dihydro-1,3-dimethyl-
28	37.824	0.58	2,7-Methanonaphthalene, 1,2,4a,7,8,8a-hexahy
29	38.088	0.70	Naphthalene, 1,2,3,4-tetrahydro-6-methyl-
30	40.230	1.44	Naphthalene, 1-methyl-
31	46.586	1.00	n-Decanoic acid
32	53.675	1.00	Pentadecane
33	63.847	1.43	9-Tricosene, (Z)-
34	64.228	0.88	8-Heptadecene
35	64.824	0.53	1-Nonadecene
36	78.937	2.33	n-Hexadecanoic acid
37	86.113	0.53	2-Cyclopenten-1-one, 2-pentyl-
38	87.480	12.23	Oleic Acid
39	87.771	1.21	Undec-10-ynoic acid, undec-2-en-1-yl ester
40	88.256	1.97	Octadecanoic acid
		100.00	

A7: Sn-MM 7 chromatograph



Peak#	R.Time	Area%	Name
1	3.426	2.12	Benzene
2	4.114	0.89	Hexane, 3-methyl-
3	6.045	8.35	Toluene
4	7.304	1.04	Hexane, 2,4-dimethyl-
5	10.216	3.17	Ethylbenzene
6	10.826	10.57	p-Xylene
7	12.014	2.79	o-Xylene
8	12.401	0.80	Cyclooctene, (Z)-
9	12.584	0.88	Nonane
10	15.896	0.98	Benzene, propyl-
11	16.445	4.04	Benzene, 1-ethyl-2-methyl-
12	16.652	3.73	Benzene, 1-ethyl-2-methyl-
13	18.731	3.67	Mesitylene
14	21.456	0.76	Indane
15	23.164	1.34	Benzene, 1,2-diethyl-
16	25.980	0.61	1-Undecene
17	26.603	0.56	Undecane
18	29.109	0.65	Benzene, 1-ethenyl-4-ethyl-
19	40.216	1.24	Naphthalene, 1-methyl-
20	53.672	1.06	Pentadecane
21	63.839	1.40	8-Heptadecene
22	64.217	1.17	8-Heptadecene
23	65.214	0.65	Heptadecane
24	74.683	0.52	Benzene, dodecyl-
25	79.022	5.72	n-Hexadecanoic acid
26	86.107	0.94	2-Cyclopenten-1-one, 2-pentyl-
27	87.622	28.45	Oleic Acid
28	87.929	2.64	cis-13-Octadecenoic acid
29	88.392	5.31	Octadecanoic acid
30	94.626	2.70	13-Docosen-1-ol, (Z)-
31	95.515	1.26	9-Octadecen-1-ol, (E)-
		100.00	