

**UPGRADING OF NIGERIAN BITUMEN USING ZEOLITE -Y BASED
CATALYST**

BY

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**DEPARTMENT OF CHEMICAL ENGINEERING,
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ZARIA NIGERIA**

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P16EGCE8032**

**A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE
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**DEPARTMENT OF CHEMICAL ENGINEERING,
FACULTY OF ENGINEERING,
AHMADU BELLO UNIVERSITY,
ZARIA NIGERIA**

JUNE, 2021

DECLARATION

I declare that the work in this dissertation entitled **UPGRADING OF NIGERIAN BITUMEN USING ZEOLITE-Y BASED CATALYST** has been performed by me in the Department of Chemical Engineering. The information derived from the literature has been duly acknowledged in the text and a list of reference provided. No part of this dissertation was previously presented for another degree at this or any other institution.

Nwosibe Patrick Ogbonna

Signature

Date

CERTIFICATION

This report entitled **UPGRADING OF NIGERIAN BITUMEN USING ZEOLITE-Y BASEDCATALYST** by PATRICK OGBONNA NWOSIBE meets the regulation governing the award of degree of Masters of Science, of the Ahmadu Bello University and it's approved for its contribution to knowledge and literary presentation.

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DEDICATION

To my lovely family, Onyinye, Ezinne, Daberechi and Ezekwesiri Nwosibe. I love you guys beyond words.

ACKNOWLEDGEMENT

All Glory to God Almighty, the maker of heaven and earth for all his mercies and for thus far He has helped me in the journey of life despite my imperfections.

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To my mum and prayer warrior, thank you mum. As you can see God answers all you ask concerning me and my family and He will do more. I love you mum and I will make you proud on the global stage before God calls you home.

ABSTRACT

Heavy crude oil is an important unconventional hydrocarbon resource that can be upgraded to useful petroleum products. Nigeria has a large deposit of bitumen and sand oil, of about 38 billion barrels mainly found around the south-west and south- south regions of the country. However, this heavy oil has some challenges due to its high viscosity, low mobility coupled with its low API gravity, these features make processing and transportation of heavy oil quite challenging. Consequently, there is need to upgrade this heavy oil using suitable technique and appropriate catalyst. In this study, an equilibrated FCC catalyst (E-CAT) was sourced from a refinery, characterized using XRD, XRF and FT-IR technique; result showed it contains active constituents required of a commercial FCC catalyst. The XRD result showed the reflection peaks at $2\theta = 7^\circ$, 10.2° , 18.7° , 25° present in zeolite-y are also found in E-CAT though in smaller amount of about 40%, XRF result showed it contains similar oxides with zeolite-y like Al_2O_3 , SiO_3 but the percentage composition is lower in E-CAT due to reduction in activity caused by coke deposits. FT-IR result followed the same pattern. It was then tested in upgrading heavy crude oil. In a preliminary work, heavy gas oil (HGO) and vacuum gas oil (VGO) were used as model oils. They were cracked in a high pressure-high temperature batch reactor at varying temperatures of 350, 400 and 450°C, initial pressure of 1MPa and catalyst-to-oil ratio of 0.01 for the catalytic reaction. Parameters studied include viscosity reduction and change in structural composition of the model oils before and after upgrading using FT-IR technique. Results of VGO upgrade showed viscosity reduction of 3.5, 10 and 32% after thermal upgrade at 350, 400, 450°C and 10, 15 and 42% after catalyst addition at the temperatures respectively. The HGO upgrading result showed viscosity reduction of 4, 7 and 24% after thermal upgrade at 350, 400 and 450°C respectively and 6, 13 and 33% viscosity reduction after catalyst addition correspondingly. FT-IR results suggest the formation of saturated hydrocarbons an indication of the formation of valuable products after upgrading reactions with a better results recorded after catalyst addition. Thereafter, the equilibrated FCC catalyst (E-CAT) was used to upgrade Nigeria bitumen from Agbaba in Ondo state. E-CAT, hydrogen gas and glycerol were added into bitumen (viscosity of 32000cSt measured at 40°C) in the batch reactor at 350°C for reaction time of two hours, pressure of 10MPa and catalyst to bitumen ratio of 0.02. Viscosity reduction after thermal upgrade were 83 and 98% at room temperature and at 40°C respectively while the reduction after catalyst upgrade were 87.9 and 98.9% correspondingly under the same conditions. It was found that there was improved API gravity from 11.6 to 26.6 which is 129% increase after thermal upgrade and 31 which is 167% increase after catalytic reaction. Other physiochemical properties of the bitumen investigated like pour point, flash point, fire point, specific gravity, and penetration point also improved significantly towards the production of lighter oil. The chemical composition of the bitumen before and after the upgrading reactions at 350°C were investigated using FT-IR and GC-MS technologies. The result shows that the heavy molecular compounds like resins and asphaltene were broken down to lighter compounds like saturates and aromatics with more positive results recorded after catalytic reactions. The overall results showed that equilibrated FCC catalyst (E-CAT) possesses the potentials to be used in heavy crude oil upgrading.

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CHAPTER ONE

INTRODUCTION

1.1 Background of Study

Due to increasing global demand for crude oil and its allied products and subsequent decline in the global reserve of conventional crude, there is the need to look for alternative source of crude oil to meet the rising global energy demand for the next decades. Heavy and extra heavy oil like bitumen are that alternatives that researchers are turning attention to globally. While it is true that there is a global effort to shift away from fossil fuel (non- renewable energy) to biofuel (renewable energy but crude oil and its allied products like PMS, AGO, LPG, etc. will continue to play a major role in the global energy demand for the next few decades and even more(Guo, *et al*, 2016). According to the Organisation of Petroleum Exporting Countries (OPEC), the global oil demand will reach 111.1million barrels per day bythe year 2040 and the current oil reserve will not meet this projection if alternative sources are not sought(Guo*et al*, 2016).

Sand oil or bitumen is anaturaloccurring extra heavy oil that requires additional,processing to extract, transport and refine into petroleum products than lighter conventional oil(Christina, 2015). As conventional oil reserve decline globally, companies are turning towards these extra heavy oil to meet global demands for petroleum products which are on the increase (Yusuf *et al*,2016).However, their inherent properties, characterized by high viscosity and poor mobility coupled with the complex configuration make the desired recovery processes very challenging.

Presently, Nigeria has an estimated 38 billion barrels of bitumen and extra heavy oil deposit; this figure is almost the same as her conventional crude oil reserve (Ogiriki et al. 2018). Nigeria has a very large sand oil (bitumen) deposit especially in South West and part of South-South regions (Christina, 2015). Unfortunately, this bitumen deposit is largely untapped due to several reasons among which are lack of technological know-how, environmental factors, lack of political will to mention a few. There is also the issue of fear by host communities due to the experiences of environmental degradation in Niger Delta region and the government unwillingness to tackle the menace.

The technologies for upgrading heavy oil are generally classified under two headings, namely surface upgrading and in-situ upgrading (Speight, 2009).

There are also other several in-situ techniques also called enhanced oil recovery methods that can be employed to recover heavy oil; most of them fall into three categories, thermal injection, gas injection and chemical injection. These techniques have their merit and limitations.

A number of researches have been conducted using different catalysts to upgrade heavy crude oil. Oil-soluble, water-soluble, dispersed and zeolite-based catalysts were all tested in upgrading heavy crude oil (Shuwa et al., 2017a; Shuwa et al., 2017b; Shuwa et al., 2015; Tian et al., 1998; Weissman & Kessler, 1996). Zeolite-based catalysts proved to be another promising alternatives in upgrading heavy crude oil due to their high activity, thermal and chemical stability, high selectivity and possession of acidic active sites that are required in cracking long chain hydrocarbons. Kuznicki et al. (2007) successfully reduced the viscosity of North America heavy oil alongside metals, nitrogen and sulfur at 400°C with natural zeolite upgraded with raw high sodium chabazite ore. They compared their results at similar conditions with thermal cracking

to attain a viscosity reduction of 88.7% for the latter and 96.7% for the former, a marked 8% difference.

Also, Junaid *et al* (2010) attempted to reduce the viscosity and upgrade Athabasca oilsands with natural zeolites like clinoptilolite and Ca-chabazite between 300 to 350 °C. Although, they reported significant viscosity reduction, less gas and coke formation and increase maltenes component at 350 °C, they recorded increased asphaltene contents for thermal and catalytic upgrading with Ca-chabazite at 300 °C. They further assessed the effectiveness of clinoptilolite and Ca-chabazite in the presence of water. In another work, Junaid *et al* (2014) asphaltenes was successfully reduced from 19.5 wt% to 11.2 wt% with clinoptilolite and 14.4 wt% with Ca-chabazite at 3 wt% water addition, on the other hand, in the absence of water their previous result was replicated with 16.2 wt% for clinoptilolite and 29.2 wt% for Ca-chabazite attributed to severe cracking and conversion to gas and coke resulting in relative reduction of the feed or alternatively dismutation of the resins fraction.

The major shortcomings of most zeolite catalysts tested in heavy oil upgrading are small pore sizes, low mechanical strength and absence of metal active sites that are required for hydrogenation reactions (Meng *et al.*, 2019; Shuwa *et al.*, 2017b).

This research work will employ one of the surface upgrading method catalytic cracking to upgrade bitumen sourced from Agbabu in Ondo State, Nigeria using an FCC-based catalyst.

1.2 Problem Statement

Many researchers have used different catalysts especially metal supported zeolite based catalyst to upgrade heavy oil. However, there is yet no established suitable catalyst for

optimal result due to small pore space of the catalysts used, low mechanical strength and the cost implication of the metals.

1.3 Aim and Objectives

The aim of this research work was to investigate bitumen upgrading using zeolite -Y basedFCC catalyst

The objectives of this study are to:

- (i) Source and characterize (viscosity, API gravity. pour point, penetration point, softening point, FT-IR, GC-MS) bitumen from Agbabu in Ondo State, Nigeria
- (ii) Characterize the equilibrated zeolite –Y based catalyst (E-CAT) using XRD, XRF and FT-IR technique.
- (iii) Perform thermal and catalytic upgrade of model oil (VGO and HGO) and bitumen, then characterize the products

1.4 ResearchJustification

Research in catalytic upgrading was not vigorously pursued in the past due to the availability of light oil also known as conventional oil. However, conventional oil production is projected to peak and decline irreversibly in the near future making unconventional heavy oil more essential for future energy need. Also Nigeria has a very large deposit of bitumen of about 38billion barrel which is untapped. This large deposit has potential to elongate the life span of Nigeria crude oil deposit which at present is the source of our foreign earning if properly harnessed and upgraded to lighter crude. Finally, zeolite –Y based catalyst is currently in use globally in most refinery in FCC unit to breakdown heavier oil fractions to obtain lighter distillates.

1.5 Research Scope

The scope of this work is limited to the upgrading of VGO, HGO as model oil and bitumen sourced from Agbabu in Ondo State Nigeria using Equilibrated Zeolite-Y based catalyst in a high pressure batch reactor at a temperature of 350°C and pressure of 10mpa. The catalyst was characterized using XRD, XRF and FT-IR techniques while the model oils and bitumen were characterized using GC-MS, FT-IR, viscosity, API gravity techniques before and after upgrading.

CHAPTER TWO

REVIEW OF LITERATURE

2.1 Background

Conventional light crude oils have high mobility due to their low viscosity, usually less than five centipoise at reservoir conditions. On the other hand, unconventional heavy crude oil and bitumen have little or no mobility in the reservoir, because of their very high viscosity which can be several orders of magnitude. Thus, in comparison, heavy crude oils are more difficult to produce and are also costlier to recover and refine. This is chiefly because of their high viscosity, low API gravity, high asphaltene, heteroatom, and heavy metals content. Heavy oil reserves are about 4–6 trillion barrels and are therefore of a similar order, or greater, than conventional light oil (Zhang et al., 2012). Canadian production of heavy crude and bitumen has risen to around 2 million Barrels of Oil Per Day (BOPD) (Sonmichsen, 2020). Venezuelan extra heavy crude is around 1 million BOPD and long running heavy oil production is approximately 600,000 BOPD, for this to increase in the future will require more advanced production strategies, including advanced Enhanced Oil Recovery.

Bitumen also occurs naturally alone or mixed with mineral matter and was first known to man seepages exuding from the ground. Pure bitumen deposit occurs in various parts of the world notably Canada, Venezuela and Nigeria.

Bitumen and extra heavy oil are unconventional oils that generally require additional processing to extract, transport, refine into petroleum product than lighter conventional oil. Bitumen is typically found surrounding sand grain encased in water and clay which is where it gets the name sand oil. The bitumen must be removed from sand and processed before it can be refined like conventional oil. Bitumen is a viscous and dense. To convert this tar-like substance into lighter oil called synthetic crude that can

be used for petroleum product such as petrol; the bitumen must be removed from the sand and processed.

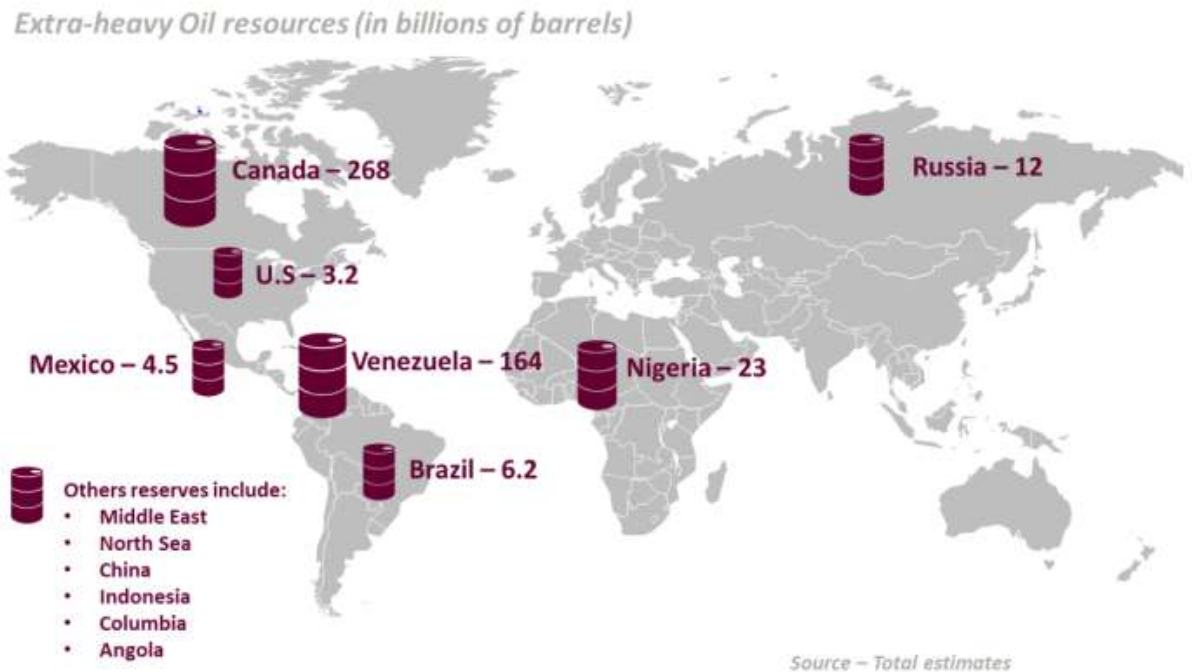


Figure 2.1: World heavy oil distribution (modified from Total Estimate, 2015)

Figure 1.1 above shows the world distribution of bitumen/extra heavy oil in billions of barrels. The chart above shows that Canada with 268 billion barrel has the highest deposit of heavy oil across the globe followed by Venezuela. Nigeria is placed third on the world table with over 23 billion barrels. Other sources confirms Nigeria has up to 38 billion barrels of bitumen/tar sand scattered majorly around the south western part of the country(Christaina, 2015).

Figure 1.2 below shows the distribution of bitumen/heavy oil/extra heavy oil in Nigeria. The areas marked block A,B and C are the regions you can find bitumen in Nigeria. They are stretched between Lagos and Benin in Edo State. Nigeria is estimated to have a vast deposit of bitumen and tar sand up to 38 billion barrels which is majorly untapped at the moment (Christaina, 2015)



Figure 2.2: Bitumen deposit across Nigeria(Christina, 2015)

2.2 Crude Oil

Crude oil is a fossil fuel formed from the remains of plants and animals which have accumulated at sediment bottoms. Over time, pressure, heat, and bacterial action transformed the deposits into hydrocarbons, water, carbon dioxide, hydrogen sulphides (Robinson, 2006). Geologically, crude oil becomes heavy via biological, chemical and physical degradation processes during migration and after entrapment inside the pore-space of the rocky reservoir. Hence, heavy oil and bitumen is formed from the residue of formerly light oil whose light molecular weight hydrocarbons components have been lost through microbial degradation, water-washing and evaporation (Meyer and

Attanasi, 2003). The U.S. Geological Survey (USGS) Energy Resource Program has classified crude oils depending on their API gravity (i.e., American Petroleum Institute) gravity and viscosity (i.e., the resistance flow) as shown in Figure 2.1. It is clear that the API gravity of heavy oil is several points lower than that of light oil. Similarly, the viscosity of heavy oil is extremely high in magnitude compared with that of light oil. Natural bitumen (or tar sands) is denser, has poor mobility, and extremely low viscosity.

2.3 Heavy Oil

This refers to the natural occurring crude that requires extra processing to be utilized. The heavy oil and extra heavy oil occur in form of mineral deposit beneath the earth surface. They are often long chain hydrocarbon substances with high boiling and melting point.

Heavy oil is a type of crude oil which is very viscous. The common characteristics properties of heavy oil are; high viscosity, high specific gravity (low API gravity), low hydrogen to carbon ratios, high carbon residue and high content of asphaltenes, high sulphur content and nitrogen. At present, heavy oil reserve makes up large portion of unconventional petroleum resources, which include tar sand and bitumen. Heavy oil production has increased substantially in the last decade as a result of market demand. This led to new technological advancement in drilling and recovery technique and a further significant increase in production will follow suit

Bitumen and heavy oil are viscous crude oil consisting of hydrocarbons and their derivatives. They are black or brown in colour and possess waterproofing and adhesive properties (Speight, 2007). By definition, heavy oils have a density between 0.93 and 1.0 g/cm³ and bitumen have a density greater than 1.0 g/cm³ (Murray Gray).

The main elemental species of bitumen are carbon (C) and hydrogen (H), followed by sulphur (S), nitrogen (N) and oxygen (O). The element compositions of bitumen from different regions vary over a relatively narrow range and the average composition is 85 wt% carbon, 13 wt% hydrogen, and a combined heteroatom (S+N+O) content of 2 wt% (Hunt, 1996). The heteroatoms are found mainly in the heaviest fraction of the oil; that is, in the residue and particularly in the asphaltenes.

Bitumen consists of millions of chemical species (McKenna and Rodgers) which can be characterized into chemical families or distillation cuts. One frequently used characterization method is SARA (saturates, aromatics, resins, and asphaltenes) analysis. In this method, the asphaltenes are precipitated from the oil and therefore are a solubility class. A generally accepted definition of asphaltenes is that they are the components that can be dissolved in toluene, but not in heptane or pentane. The other fractions are separated by liquid chromatography and therefore are adsorption classes. The saturates consist of paraffinic and naphthenic components. The aromatics, resins, and asphaltenes are a continuum of aromatic species of increasing molecular weight, density, aromaticity, polarity, and heteroatom content (Speight, 2014).

It is clear that the API gravity of heavy oil is several points lower than that of light oil. Similarly, the viscosity of heavy oil is extremely high in magnitude compared with that of light oil. Natural bitumen (or tar sands) is more dense, has poor mobility, and extremely low viscosity. The photographs in Figure 2.1 illustrate the physical characteristics of light oil, heavy oil and oilsand.

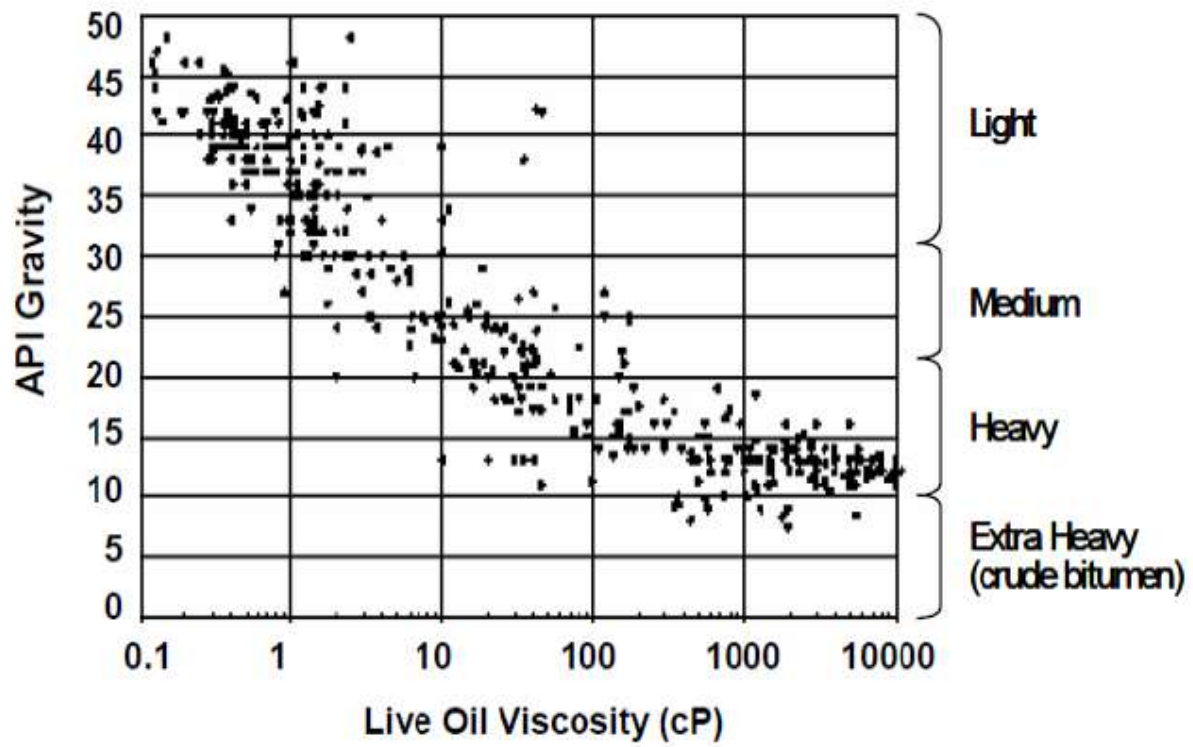


Figure 2.3: Crude oil classification based on API gravity and viscosity (Smalley, 2000)

2.3.1 Composition of Heavy Oil

The crude oil composition and properties vary with location, origin and type. Heavy crude oil and bitumen are a complex mixture of about 10^5 - 10^6 different hydrocarbon components (Wiehe, 1999). Notwithstanding, heavy crude oil components can be classified into four components: saturates, aromatics, resins, and asphaltenes collectively called SARA, as illustrated in Figure 2.2

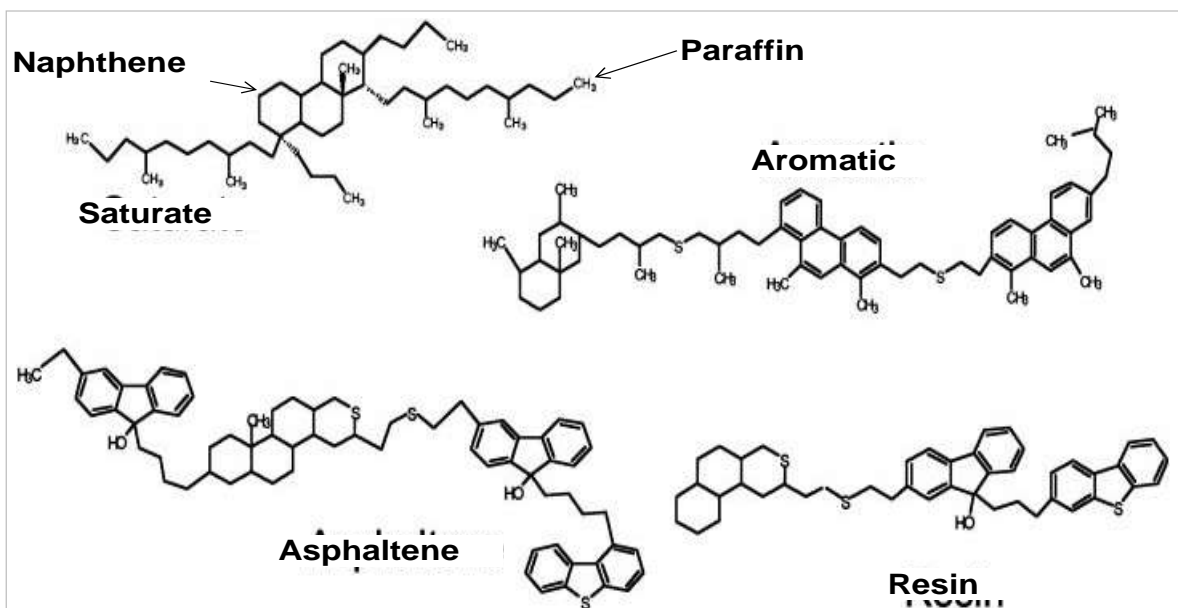


Figure 2.4. Molecular structures illustrating SARA components of heavy oil (Strauz and Lown, 2003)

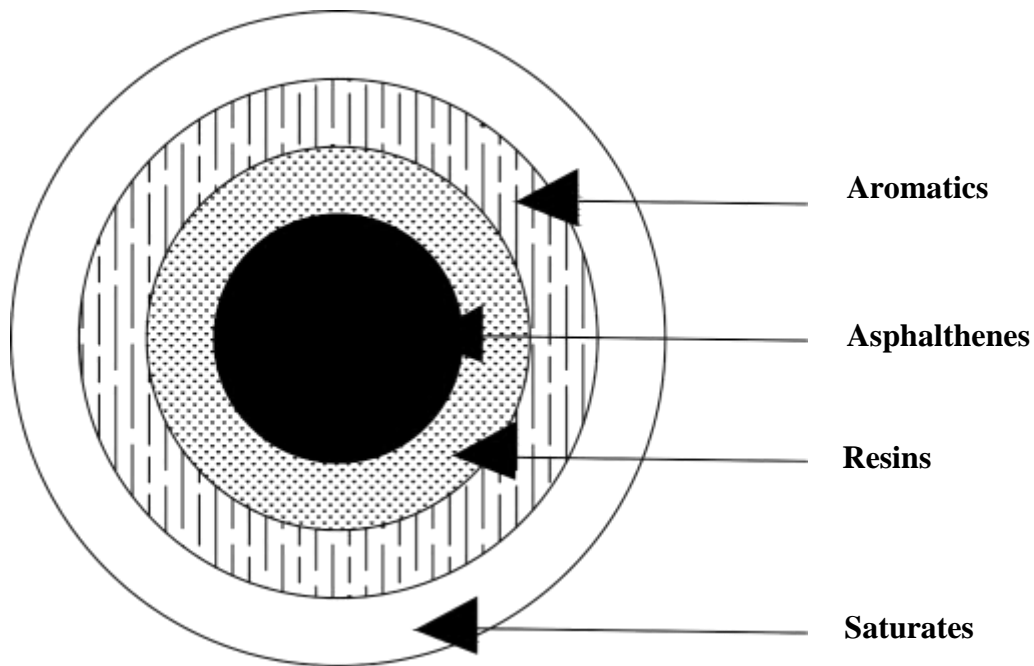


Figure 2.5: Micro-emulsion of crude oil SARA components (Modified by Nwosibe, 2021)

A micro-emulsion model involving the above four components present in the crude oil was proposed by Wiehe and Liang (1996). In the model, asphaltene occupies the core of micelles dispersed by the surfactant-like properties of resin that have been adsorbed on their surface, which are held in solution by aromatic, as shown in Figure 2.3 (Wiehe and Liang, 1996; Leyva, et al., 2007).

Saturates are a fraction of the heavy oil consisting of non-polar hydrocarbons with linear, branched, and cyclic structures saturated with hydrogen. They include paraffins (i.e., saturated straight and/or branched chains hydrocarbon) and naphthenes (i.e., cyclic saturated hydrocarbon with one or more rings and in some case with paraffin side chains, as shown in Figure 2.2). Moreover, a high proportion of saturates in the crude oil indicates an increase in the yield of lower molecular weight or lower boiling point

fractions.

Aromatics are hydrocarbons with one or more unsaturated benzene rings fused together. They may be linked with paraffinic side chains and/or a naphthenic ring as shown in Figure 2.3. However, saturates and aromatics are light components compared to resins and asphaltenes, which implies that light crude oil contains high percentage of these components.

Asphaltenes and resins are the heaviest components of the crude oil; as such the heaviness of crude oil can be linked to the high proportion of asphaltenes compared to light crude oil (Alvarez-Ramirez, et al., 2006). Resins are polar poly-aromatic molecules containing heteroatoms such as nitrogen, oxygen, or sulphur. They are soluble in light alkanes such as n- hexane, n-heptane, etc. with molecular weight less than 1000 g.mol⁻¹. Asphaltenes are composed of aromatic polycyclic clusters linked with one or more aliphatic (or naphthenic) structure (Alvarez-Ramirez, et al., 2006)

2.3.2 Upgrading of heavy oil

Several methods for bitumen upgrading are used by researchers, including atmospheric distillation and vacuum distillation, catalytic cracking, catalytic reforming, hydrocracking, and delayed coking (Mohan ,2006). Atmospheric and vacuum distillation are physical processes where raw materials are separated into fractions, each with a different boiling point range. These fractions are sent for subsequent processing, and; therefore, atmospheric and vacuum distillations are known as crude oil primary processing.

Hydrocracking is a reactive process in the presence of high pressure hydrogen and suitable catalysts. The heavy molecules in the feedstock are converted into lighter ones,

such as gasoline, kerosene, diesel oil and lubricating oil. Hydrogen is added to reduce coke formation and remove the sulphur and nitrogen atoms.

The carbon to hydrogen atomic ratio in heavy oils is often higher than that of light oils including gasoline and diesel. There are two main reaction pathways through which heavy oil upgrading occur. In the first pathway, carbon is rejected as coke to produce light oil of low carbon-to-hydrogen ratio. The other route is via hydrogen addition to favour the yield of liquid product while suppressing coke formation (Speight, 2004). The objectives of these processes are to produce more valuable light crude oil that meets refinery specifications and has minimized heavy metals and sulphur content.

The first reaction approach is often realized by thermal cracking, which removes the sided chains, break the long carbon chains into shorter ones, lower the molecular weight and reduce the viscosity. The free radical mechanism for the thermal cracking process was established decades ago (Greensfelder, 1949). A molecule becomes a free radical by losing a hydrogen atom upon collision at high temperatures leaving an unpaired electron. Unless they are rapidly stabilized, free radicals can combine to form large molecules and eventually coke. Coke formation is suppressed in the presence of a hydrogen donating liquid, which acts as the radical scavenger (Greensfelder, 1949). Therefore, a hydrogen donor can be introduced to the reaction matrix during the thermal-catalytic upgrading of heavy oil to form low molecular weight light oil without severe coke formation.

2.3.3 Chemistry of heavy oil upgrading

Heavy crude oil and bitumen are complex mixtures of about 10^5 - 10^6 different hydrocarbon components (Wiehe, 1999). Therefore, the chemistry of heavy crude upgrading is complicated, because of the many complex reaction mechanisms involved in the thermal and catalytic upgrading to syncrude. The two main reaction routes to

upgrade heavy crude oil to synthetic light crude oil either carbon-rejection and/or hydrogen-addition, with or without catalyst, basically driven by thermal energy (Heck and Diguseppi, 1994). The overall aim is to improve H/C atomic ratio, decrease heteroatom (e.g., S, N, etc.) and metals (e.g., Ni, V, Fe, etc.), lower the viscosity, and increase the yield of distillates. Consequently, upgrading occurs as a result of bond breaking. The most significant bond dissociation that leads to upgrading is the cleavage of C-C bonds.

Furthermore, Hsu and Robinson (2006) outlined the numerous possible chemical reactions that occur during upgrading, they include: homolytic cleavage of C-C bonds, side chain fragmentation (or cleavage), ring growth, hydrogen shuttling, hydrogenation of aromatic/dehydrogenation of cycloparaffins, ring opening, heteroatom and heavy metals removal. It is believed that the reaction mechanism during upgrading proceeds via the formation of free radicals, as a result of the cleavage of C-C bond through free radical chain reactions (Gray, 1994). Other reactions that take place in upgrading include thermal and catalytic cleavage of C-C, C-S, and C-N bond dissociation (McMillan, et al., 1994; Rahimi and Gentzis, 2006).

The dissociation energies of the common bonds found in the crude oil is presented in Table 2.1

Table 2.1: Bond dissociation energy (Rahimi and Gentzi, 2006)

Bond	Kcal/mol
H-H	103
C-C	83-85
C-H	96-99
N-H	93
S-H	82
O-H	110-111
C=C	146-75
C-N	69-75
C-S	66
Ar-CH ₂ -CH ₂ -Ar	71
Ar-H	111

*Ar is an aromatic hydrocarbon

From Table 2.1, it is clear that C-S has the lowest bond dissociation energy; therefore it will easily break at low temperatures

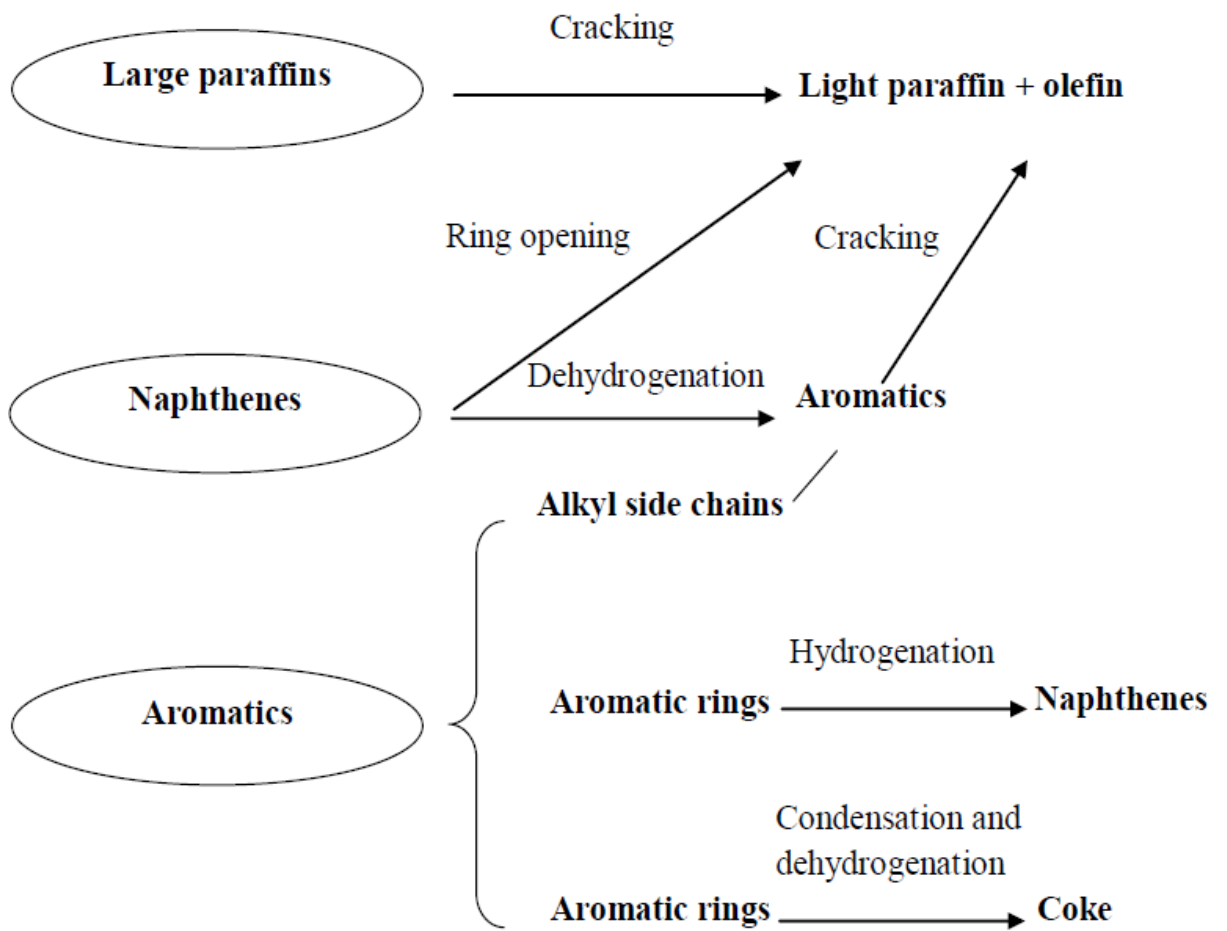


Figure 2.6 Mechanism of heavy oil upgrade(Ting *et al*,2015)

molecules to carbocations takes place in the chain propagation stage, yielding carbenium ions steadily. In some cases, the generated carbenium ions undergo isomerisation to stable secondary or tertiary carbenium ion through hydride shift or alkyl shift (Lee, et al., 2011). However, the produced carbenium ions could split to various smaller hydrocarbons through β -scission, hydride transfer, isomerisation, cracking, alkylation/dealkylation, protonation/deprotonation, ring opening (i.e., naphthenic), cyclisation, etc. In the termination stage the carbonium ions are deprotonated from the catalyst, collapse to give light hydrocarbons and/or hydrogen, and tri- co-ordinated carbenium ions (Jian-hong, et al., 2012).

2.4 Catalyst

Catalysts are substances which have the ability to alter (speed up or even slow down) the rate of chemical reaction but remains unchanged at the end of the reaction process. This is because the catalyst creates alternative pathway for the reaction process by lowering the activation energy of the process. The science and technology of catalysis is of great importance as it affects our daily lives. Four major sectors of the world economy depend highly on catalysis namely Petroleum and energy sector, food industry, pollution control, chemical and polymer production.. Catalyst are used in the production of fuel such as petrol, gasoline, diesel etcetera, Also the production of plastics fibre, synthetic materials involves catalytic process. The production of clean energy from renewable sources, production of pharmaceutical products like drugs are all possible with the aid of a suitable catalyst.

More than 80% of industrial processes uses catalyst in one form or the other. This is because of the expanding need of mankind which necessitate increased rate of production of goods and services which catalyst play a major role in this. Increased

catalyst life and catalyst upgrading are major areas of importance in maximizing catalyst efficiency.

2.4.1 Zeolite

Zeolites, also known as molecular sieves, are a group of crystalline solid catalyst with open 3D framework structures made of silicon, aluminium and oxygen (John, 2001). These atoms form $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedral, which are linked with each other by sharing all the oxygen atoms at the corners to form regular intra-crystalline cages, cavities and channels, resulting in infinite structures (Richard, 1995). A rich variety of morphologies are generated by varying the assembling manner of these platforms. At present, there are more than 231 unique zeolite frameworks found, but only over 40 naturally zeolite frameworks are under extensive research (Mohamed, 2015). The structure is neutral when it is consisted of pure silicon and oxygen tetrahedral. When some $[\text{SiO}_4]^{4-}$ tetrahedra are replaced by $[\text{AlO}_4]^{5-}$ tetrahedral, however, cations are required to balance the extra negative charge. Cations or small molecules may reside in channels and cavities inside of the framework (Richard, 1995). Many zeolites are extensively used in many parts of the world in industry and medicine, which is closely related to their unique morphologies that allow certain molecules to enter the pores and channels, where catalytic sites are located (Wei, 2015).

Zeolites have been used to do the separations and purifications in industry since the middle 50s. They are now used in a variety of applications because of their unique porous properties (Geological Survey, 2008), such as petrochemical cracking, water softening and purification, separation and removal of gases and solvents, agriculture, animal husbandry and construction. They are also widely used as catalyst support

material due to their porous structure as well as the presence of Brönsted acid sites along with Lewis acid sites (Jacques, 1979).

2.4.2 Zeolite Y

Zeolite Y is essentially used as a Fluid Cracking **Catalyst** (FCC) of heavy petroleum distillates, for increasing the yield of gasoline and Diesel fuel from crude oil (Kung et al. 2000). Zeolite Y, together with zeolite X, belongs to the family of aluminosilicate molecular sieves with a faujasite-type structure (FAU), which is characterized by the basic formula $(Ca, Mg, Na)_29 (H_2O)_{240} [Al_{58} Si_{134} O_{384}]^-$ FAU (Baerlocher 2007).

Faujasite is a rare zeolite, although its synthetic counterparts Linde X and Linde Y are largely used as sorbents and catalysts. Zeolite Y has a higher Si/Al atomic ratio than zeolite X (typically in the range 1–1.5). Therefore, the higher content of silica confers zeolite Y with higher thermal stability. The 2-4-tetrahedracuboctahedral units (sodalite cages) in the FAU framework type are arranged in the same way as the carbon atoms in diamond. They are connected via hexagonal prisms (double 6-rings) forming a 3-dimensional porous channel structure along [110], characterized by 12-oxygen ring window openings with the aperture of 8 Å and supercages of approximately 12 Å (McCusker and Baerlocher 2001).

E-CAT is an equilibrated form of zeolite -Y catalyst. It is not a spent catalyst as it were. It is mainly used in the fluid catalytic cracking unit (FCC) of a refinery. E-CAT is a catalyst that has been stabilised on the cracking process so as to give the desired result in FCC unit of a refinery. The FCC unit of the refinery is a secondary unit where heavy distillates are broken down to light products. Unlike atmospheric distillation and vacuum distillation which is a physical process, FCC is a chemical process. The FCC

takes VGO and similar streams and crack them using heat in the presence of a catalyst. The main products of FCC unit are gasoline and distillate fuels. The fresh catalyst also called F-CAT is solid like material that is made fluid by hot vapour and liquid fed into the FCC unit, because the catalyst is fluid, it can circulates around the FCC moving between reactor and regenerator vessels. The catalyst and heat break apart large molecules of gas oil into smaller molecules that make up gasoline, distillate and other higher- value product like butane and propane. After the heavy gas oil is cracked through contact with the catalyst, the resulting effluent is processed in fractionators which separates the effluent based on various boiling point into various intermediate products, including butane and lighter hydrocarbons. Carbon is deposited on the catalyst during cracking process. This carbon, known as catalyst coke, adheres to the catalyst reducing its ability to crack the oil. The coke on the spent catalyst is burnt off, which reheats the catalyst to add heat to the FCC process

2.5 Related Works

Many researchers have used different catalyst in upgrading bitumen and heavy oil (Jingjing et al., 2019; Meng *et al*,2019; Maldonado *et al*,2018). Among them zeolite based catalyst has proved to be more effective in heavy oil upgrade (Jingjing *et al.*, 2019). Application of alkali treated Fe/ZSM-5 in upgrading of heavy oil with glycerol and a hydrogen source by Jingling *et al*, 2019 saw an optimal viscosity reduction of 81%,this was directly linked to the broken down of resins in the heavy oil. Also Meng et al, 2019 used a novel zeolite which is a combination of Zeolite-Y/nano ZSM-5 to form a composite to upgrade heavy oil to lighter crude, result shows a higher yield of lighter fraction such as gasoline and liquefied petroleum gas. Maldonado *etal*2018 successfully upgraded heavy oil using NiFe nanaocatalyst and hydrocracking method, result shows improved API gravity from 13.1 to 18.3 chiefly due to asphaltene

reduction in the heavy oil. In all these, there is however no exact known catalyst for optimal yield of light oil during catalytic upgrading reaction. Fluid Catalytic Cracking FCC catalyst has been effectively used in refinery operations worldwide to crack heavy molecular compounds to yield light gasoline.

A successful upgrading of Athabasca bitumen (9.5API) using ultra-dispersed catalyst has been conducted. Result shows that the catalyst enhanced the recovery of the oil by API increase, viscosity reduction, sulphur and other heteroatoms removal (Hashemi & Nassar, 2014; Hashemi & Pereira-Almao, 2011).

Significant upgrading was reported for heavy oil in Argentina (Cavallaro, *et al.*, 2005). In a batch reactor study using $\text{Fe}_3(\text{CO})_{12}$ as a catalyst and hydrogen gas, viscosity of a heavy oil was reduced from 500 pa.s to 1.3 and sulphur was reduced by 14% (Ovalles *et al.*, 2003). A study using saponite – found the catalyst to be active for the upgrade. When such catalyst was promoted by Pt-Rh, better performance was exhibited. Saturate amounts increased from 37.5% to 47.8% while sulphur removal was increased from 58.6% to 69.6% on the unprompted and promoted catalyst respectively (Al-Salah *et al.*, 2004)

Upgrading of a local Canadian bitumen from Alberta region was performed in a batch autoclave reactor at a hydrogen pressure of 3.45 Mpa, 380°C temperature and reaction times varying from 3 to 70 hours. Submicro Ni-W-Mo catalyst was used for the reaction. Result showed that the catalyst enhanced the upgrading of Athabasca bitumen by effectively hydrogenating the liquid product thus helping coke formation and improved viscosity and API gravity (Galarrage & Pereira-Almao, 2010).

It is considered that around 90% of crude oil chemical composition mainly consists of hydrocarbons such as naphthenes, parafins and aromatics. The remaining 10 % is composed by molecules that, at least, contained one heteroatom like nitrogen, sulphur

and oxygen (NSO), and metals such as vanadium and nickel, which are difficult to characterize due to their low concentration and high boiling points (Hughey *et al.*, 2002; Hughet *et al.*, 2004). The identification and characterization of these compounds is critical as they are associated with different operational problems within production, transportation, refining and storage of crude oil and its by-products. Different analytical techniques for the characterization of the compositional diversity of these samples, including High Performance Liquid Chromatography (HPLC) and two-dimensional Gas Chromatography (GCxGC), are usually employed to characterize crude oil fractions (Reddy *et al.*, 2007). Despite HPLC have been used to analyse heavy oils and vacuum residue fractions (Ueda *et al.*, 1991), conventional chromatographic techniques allow addressing just bulk physicochemical properties and have a better performance with low boiling point fractions due to the samples complexity that exponentially rises as their boiling points increase. Additional techniques such as Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared (FTIR) and X-ray Photoelectron Spectroscopy (XPS) are also used for compositional characterization but, generally previous separation and fractionation are needed (Pruski, *et al.*, 1998; D'Alessio, Vergamini & Benedetti, 2000). Techniques such as Gas Chromatography (GC), Supercritical Fluid Chromatography (SFC), among others have been coupled to Mass Spectrometry (MS) to provide detailed characterization of crude oil composition (Damsté *et al.*, 1999). However, GC and SFC are conceived for petroleum distillates including heavy fractions (Dutriez *et al.*, 2010), while SFC has shown very poor resolution capability for residual samples (Dutriez *et al.*, 2013).

Polar molecules in petroleum were first studied using Electrospray Ionization (ESI) mass spectrometry by Zhan and Fenn (2000), because ESI selectively ionizes acidic and

basic polar heteroatom containing compounds; however, deficient resolution power for complete composition.

CHAPTER THREE

MATERIALS AND METHOD

This chapter describe the research methodology, procedure, materials, chemicals and instruments used in the upgrading of HGO, VGO and bitumen. It also describes the method of determining the composition and characteristics of the raw and upgraded heavy oils.

3.1 Materials and Equipment

The following materials and equipment were used in the course of this study:

Table 3.1: List of Materials

S/N	Materials	Source
1	Raw bitumen	Agbabu in Ondo State
2	High Gas Oil (HGO)	KRPC, Kaduna
3	Vacuum Gas Oil (VGO)	KRPC, Kaduna
4	Equilibrated Catalyst	KRPC, Kaduna
4	Hydrogen gas	BOC Gas LTD
5	Tetra chloromethane (TCM)	Guangdong Gaunghua Sci-Tech Co.Ltd,China

Table 3.2: List of Major Equipment Used

S/No	Equipment	Model/year	Availability
1	High Pressure - high temperature Parr batch reactor	Parr/2018	PTDF Lab, Dept. of Chemical Engineering, ABU
2.	XRF thermos scientific Niton analyser	XL3t 950	Step-B Lab, Kaduna Poly.
3	Weighing Balance	WT 500029	PTDF Lab Dept. of Chemical Engineering, ABU
4	Digital Viscometer	DV-1	Physics Lab Dept. of Physics, ABU
5	FTIR Machine	CAIY 630	Chemistry Lab Dept. of Chemistry, ABU
6	GCMC	Variant 3800	Chemical Engineering Lab, ABUAD
7	XRD Machine	Rigaku miniflux II	Analytical Lab NARICT,
8	Viscometer Bottle	-	Highway Lab Dept. of Civil Engineering, ABU
9	Specific Gravity Bottle	-	Highway Lab Dept. of Civil Engineering, ABU
10	Cleveland Open Cup	-	Highway Lab Dept. of Civil Engineering, ABU

3.2 Methodology

The experimental procedure started with the characterisation of raw bitumen and catalyst, thermal and catalytic upgrading of the model compounds (HGO and VGO), bitumen and characterisation of products formed.

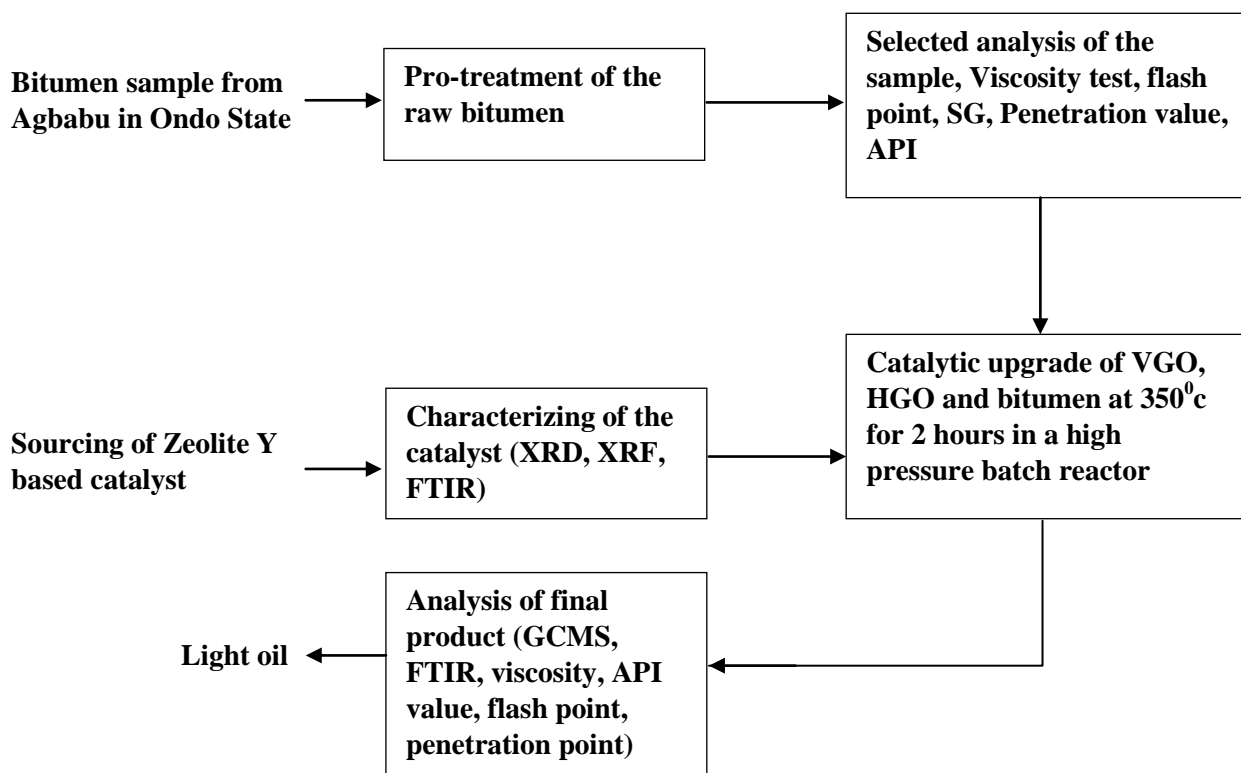


Figure 3.1 Flow diagram of the catalytic upgrading of model oil and bitumen

3.2.1 Viscosity test of bitumen

Viscosity is reverse of fluidity. It is a measure of the resistance to flow. The higher the viscosity of liquid bitumen, the more nearly it approaches a semi-solid state inconsistency. Saybolt Furol viscosity test is used to determine viscosity of liquid bitumen. While the viscosity of the upgraded bitumen, VGO and HGO was determined using a digital viscometer DV-1.

Procedures:

The cork was being inserted in the bottom of the viscometer cup and filled with the prepared sample to such a height that the levelling peg on the value is just immersed when the water is vertical. The cork was inserted, provided with central hole and a groove at one side through which the stem of the value may be passed into the upper end of the cup and pass a thermometer through the central hole so that its bulb is

approximately at the geometric centre of the sample. Then the cup was suspended up to its rim in a water bath maintained at 0.10°C of the test temperature for a period of 1.5hrs.

The viscometer was set up in a level position, fill the bath with water and adjust its temperature to within 0.10°C of the test temperature. Throughout the test the bath temperature was maintained at the same temperature value and stirring frequently.

The cup was placed in the viscometer water bath and the sample was checked to ensure that the temperature has reached the required temperature of the thermometer NN77 and corks.

Excess sample was removed so that its final level is on the centreline of the levelling peg when the value is vertical.

Mineral oil was poured into the receiver up to 20ml graduation mark and then placed the receiver directly under the orifice of the cup. Lift the valve and suspend it on the valve and suspend it on the valve support. The time recording device was started when the liquid in the receiver reached the 25ml graduation mark and stop it when the liquid reaches 75ml graduation.

3.2.2 Specific gravity test of bitumen

This test is done to determine the specific gravity of semi-solid bitumen road tars, creosote and anthracene oil as per IS: 1202 - 1978. The principle is that it is the ratio of mass of a given volume of bitumen to the mass of an equal volume of water, both taken at a recorded/specified temperature.

Procedure

The specific gravity bottle was cleaned, dried and weighed along with the stopper (W_1). It was filled with freshly boiled distilled water and inserted the stopper firmly. We kept it in the water bath having a temperature of $27.0 + 1^{\circ}\text{C}$ for not less than half an hour

and weighed it (W_4). Next the specific gravity bottle was weighed about half-filled with the material (W_2).

Then the specific gravity bottle was weighed and half-filled it with the material and the other half with distilled water (W_3). Lastly the specific gravity bottle was weighed completely filled with the material (W_5).

Specific gravity (SG .G.) =3.1

Where

$$\frac{W_2 - W_1}{(W_4 - W_1) - (W_3 - W_2)}$$

W_1 is weight of empty flask

W_2 weight of flask + sample

W_3 weight of flask + sample + water

W_4 weight of flask + water

3.2.3 Flash point and fire point tests of bitumen

Flash point of bitumen is the temperature at which, its vapour will ignite temporarily during heating, when a small flame is brought into contact with the vapour. The knowledge of this point is of interest mainly to the user, since the bitumen must not be heated to this point. The flash point tells the critical temperature at and above which suitable precautions are required to be taken to eliminate the danger of fire during heating. This temperature, however, is well below that at which the bitumen will burn. The latter temperature is called the fire point.

Flash point:

It is the lowest temperature at which the vapour of a bituminous material momentarily takes fire in the form of a flash, under specified conditions of test..

Procedure

To determine the Flash and Fire Point of Bitumen

The bitumen was softened between 75 and 100°C. It was then stirred thoroughly to

remove air bubbles and water. The cup was filled with the material to be tested up to the filling mark; it was then placed on the bath, the open clip was then fixed and the thermometer of high or low range as per requirement was inserted and also the stirrer to stir it.

The test flame was lighted and adjusted. Heat was supplied at such a rate that the temperature increased, recorded by the thermometer was neither less than 5°C nor more than 6°C per minute.

Open flash point was taken at that temperature when a flash first appeared at any point on the surface of the material in the cup. We took care that the bluish halo that sometimes surrounds the test flame was not confused with the true flash. The stirring was discontinued during the application of the test flame. The flash point was taken as the temperature read on the thermometer at the time the flash occurred.

Fire point

After flash point, heating was continued at such a rate that the increase in temperature recorded by the thermometer was neither less than 5°C nor more than 6°C per minute.

The test flame was lighted and adjusted so that it is of the size of a bead 4mm in diameter.

The flash point was taken as the temperature read on the thermometer at the time of the flame application that caused a distinct flash in the interior of the cup.

The fire point was taken as the temperature read on the thermometer at which the application of test flame caused the material to ignite and burn for at least 5 seconds.

3.2.4 Bitumen penetration test

This is a basic test for determining the grades of bitumen.

The penetration of bituminous material is its consistency expressed as the distance in

tenths of a millimeter that a standard needle penetrates vertically into a specimen of the material under specified conditions of temperature, load and duration of loading. Grades of straight-run bitumen are designated by two penetration values, for example, 40/50, 60/80, 80/100 etc.; the penetration of an actual sample of the bitumen in any grade should fall between the lower and upper value given.

Procedure:

The needle was being examined for damage or surface roughness; it was wiped with a cloth soaked in toluene and then dried with a clean cloth. The clean needle was inserted into the penetrometer apparatus and the total sliding weight made up to the required value, by adding additional weights. The sample container is then placed in the transfer dish complete with water at the required temperature from the constant temperature bath, the sample being completely covered with water at all times. The transfer dish is then placed on the stand of the apparatus.

3.2.4 API gravity

American Petroleum test is almost the most important test carried on bitumen and crude oil globally. This is because bitumen and crude oil generally are rated globally based on their API index. An oil with low API gravity has high viscosity and is regarded as low quality whereas oil of high API gravity with low viscosity is of high quality .refer to Fig 2.1 for the API/viscosity chart. The API gravity was determined or calculated as shown below.

Determination of API gravity

$$API = 141.5/SG - 131.5$$

$$\text{For raw bitumen} = \frac{141.5}{SG} - 131.5$$

$$\text{For thermally upgraded oil} = \frac{141.5}{SG} - 131.5$$

For catalytically upgraded bitumen = $\frac{141.5}{SG} - 131.5$

To calculate the specific gravity SG, the following formula was used

$$\text{Specific gravity (S.G.)} = \frac{W_2 - W_1}{(W_4 - W_1) - (W_3 - W_2)} \dots\dots\dots 3.2$$

Where

W₁ is weight of empty flask

W₂ weight of flask +sample

W₃ weight of flask + sample + water

W₄ weight of flask + water

3.2.5: Pour Point

Pour Point was determined using the automatic ASTM D5949 Standard Test Met

3.3 Catalyst characterization

X-ray diffraction (XRD) was carried out using a Rigaku miniflux II X-ray diffractometer with Cu k radiation. The anode operated at 40Kw and 40mA X-Ray. The catalyst was scanned in a continuous mode at wavelength K_{alpha} =1.540562 and K_{beta} =1.3922182, 2 Θ from 20° to 50° at scanning speed of 12°/min. The pattern was compared to that of commercial zeolite-Y catalyst procured commercially from Zeolyst international.

The functional group of the catalyst was analysed by FT-IR. The FTIR analysis was carried out by placing 1mg of samples on an Agilent CAIY 630 FTIR machine. The spectrometer directs beams of Infra-Red (IR) at the sample and measured how much of the and at which frequencies the sample absorbs the infrared light. The reference data base housing thousands of spectra was identified.

X-ray Fluorescence was carried up using an XRF thermos scientific Niton analyser with model number XL3t 950. The sample was irradiated with high energy X-ray from a controlled X-ray tube

3.4 Upgrading of Model Compounds

3.4.1 Cracking of high gas oil (HGO)

A volume of 200 ml of high gas oil (HGO) was measured in a 250ml Pyrex measuring cylinder. The HGO was poured into the stainless container of the reactor and the lid tightened at uniform pressure (0.00005bar). The reactor is a high pressure batch reactor made of stainless steel, with volume of 500ml and temperature rating of not more than 500°C and maximum pressure of 10 mPa. It is made of the reactor component and the control panel. The reactor components comprises of the reactor vessel surrounded by the heating element, a gas inlets and outlet, a pressure gauge and a magnetic stirrer; the control panel consist of the power switch and a control knobs from where the heating and stirring components are controlled and monitored Nitrogen gas were pumped into the system at initial pressure of 6bar to keep the system inert. The temperature was set at 350 °C and heating allowed for 2 hours. The temperature and pressure readings were taken every 10minutes interval throughout the experiment. There after the system was shut down and allowed to cool to near room temperature before the content was removed and taken for analysis The procedure was repeated with temperature set at 400 °C and 450 °C respectively . Again the whole process was repeated with the addition of 2g of equilibrated catalyst which was weighed using a WANT electronic

weighing balance to get the effect of catalyst on upgrading the high gas oil. stirring was done at 12rpm to ensure homogeneity of the mixture of oil and catalyst.

3.4.2 Cracking of vacuum gas oil (VGO)

A volume of 200 ml of Vacuum gas oil (VGO) was measured in a 250ml pyrex measuring cylinder. The VGO was poured into the stainless container of the reactor and the lid tightened at uniform pressure (0.00005bar) Nitrogen gas was pumped into the system at initial pressure of 6bar. The temperature was set at 350 °C and heating allowed for two hours reaction time. The temperature and pressure readings were taken every 10minutes interval throughout the experiment. There after the system was shut down and allowed to cool to near room temperature before the content was removed and taken for analysis The whole procedure was repeated with temperature set at 400 °C and 450 °C respectively with other conditions kept constant .

For catalytic upgrading process, 2g of equilibrated catalyst was measured and weighed in WANT electronic balance and poured into the reactor containing 200ml of VGO, the mixed was stirred at 120rpm for homogeneity of the mixture. The same temperature and reaction time was maintained as in the thermal process described earlier.

3.4.3 Characterization of upgraded model oil

Change in functional group of the HGO and VGO before and after upgrade was analysed using FT-IR technique. The FT-IR analysis was carried out by placing a samples in FT-IR spectrometer. The spectrometer directs beams of IR at the sample and measured how much of the beam and at which frequencies the samples absorbs the infrared light. The viscosities of the raw and upgraded heavy oil were determined using the DV-1 digital viscometer machine.

3.5 Upgrading of Bitumen

A mass of 100 g of raw bitumen was measured and charged into the high pressure batch reactor. The reactor is a high pressure batch reactor made of stainless steel, with volume of 500ml and temperature rating of 500°C and maximum pressure of 10 mPa.. 2 g of commercial FCC equilibrated catalyst (E-CAT) from zeolyst was weighed and poured into the reactor; 10 ml of glycerol was also added before closing the reactor .The set up was pressurized with hydrogen to an initial pressure of 6bar after which the hydrogen sourced was disconnected. The reactor was then switched on with the stirrer set at 120rpm and temperature at 350°C. Temperature and pressure readings were taken at 10 minutes intervals. The reaction was allowed to proceed for 2 hours after attaining the set temperature before the reactor was turned off and allowed to cool. The product of the reaction was then collected for analysis. The thermal experiment was carried out the same way except that there was no catalyst addition as in the catalytic upgrading reaction described above.

3.5.1 Characterization of upgraded bitumen

Changes of functional group in the bitumen before and after upgrade were analysed by FT-IR

GC-MS analysis was carried out using a Varian 3800 gas chromatograph equipped with a Agilent MS capillary column (30 m × 0.25 mm i.d.) linked to a Varian 4000 mass spectrometer functioning in the EI mode (70 eV; m/z 1 – 1000; source temperature 230°C and an increase fourfold temperature 150°C). The column temperature was originally kept at 200°C for 2min, increased to 300°C at 4°C/min, and retained for twenty minutes at 300°C. The transporter gas was Nitrogen at a flow rate of 1.0 mL/minutes. The inlet temperature was kept at 300°C with a split ratio of 50:1. A model volume of 1µL in chloroform was added using a split mode, with the split ratio of 50:1. The mass spectrometer was set to scan in the range of m/z 1-1000 with electron

impact (EI) mode of ionization, runtime were forty minutes. Using computer searches on a NIST Ver.2.1 MS data library and likening the spectrum obtained through GC – MS compounds existing in the samples were recognized.

The viscosity of the upgraded bitumen was determined using the DV-1 digital viscometer machine.

Penetration point test was carried out using the ASDM-95-D7 semi-automatic penetrometer BO57-10, a thermometer, a time measuring device and a water bath maintained at $25^{\circ} \pm 0.1^{\circ}\text{C}$. Flash point and fire point were determined using the SYD-3536 Cleveland Open-Cup Apparatus with a cup, thermometer and Bunsen burner. Pour Point was determined using the automatic ASTM D5949 Standard Test Method.

The specific gravity and API gravity was calculated as shown below

Determination of API gravity

$$\text{API} = 141.5/\text{SG} - 131.5$$

For upgraded oil, $\text{API} = \frac{141.5}{\text{SG}} - 131.5$, where SG is Specific gravity

The coke and asphaltene content of the bitumen before and after upgrade was determined. The amount of coke produced after upgrading was obtained by dissolving 1.0g of the resulting synthetic crude in 40ml Dichloromethane. The mixture was stirred for 10minutes and stored away from sunlight for 24hours. After the 24hours it was centrifuged for 20minutes and the precipitates weighed (Onoriode *et al.*, 2018).

The asphaltene fraction was removed by dissolving 500mg of crude in 40ml n-heptane. The solution was stirred and allowed to stand for 24hours after which the precipitate was filtered using a filter paper and weighed.

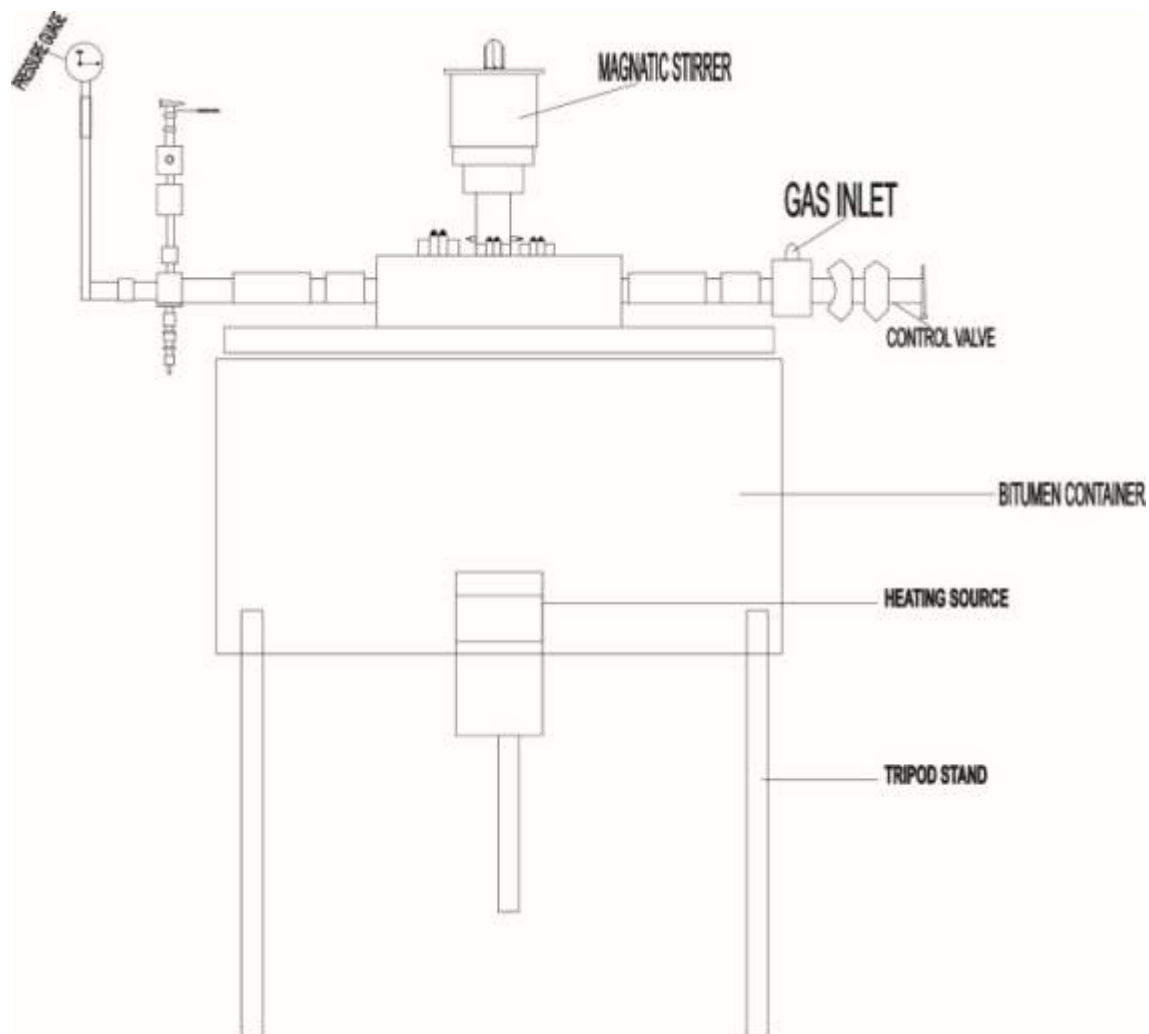


Figure3.2: Schematic diagram of the high-temperature high-pressure batch reactor

3.6 Analyses

3.6.1 Fourier-Transform Infrared Spectroscopy (FT-IR)

The result of the FTIR analysis and its discussion is presented in chapter four.



Plate 1:FT-IR Machine model CY630

3.6.2 Gas Chromatogram –Mass Spectrometer (GC-MS)

The result of the GC-MS analysis and its discussion is presented in chapter four



Plate 2: GC-MS Machine

3.6.3 X-Ray Fluorescence

X-ray Fluorescence was carried up using an XRF thermos scientific Niton analyser with model number XL3t 950.

CHAPTER FOUR

RESULTS AND DISCUSSION

This chapter presents the results of analysis and their discussion for the experimental procedure employed in this study.

Mm 4.1 Results

4.1.1 Physiochemical analysis of raw bitumen

The characterisation tests carried out and results obtained are presented in the tables below

Table 4.1: Physiochemical Analysis of Raw Bitumen

S/N	TEST	LAB.	LITTERATURE
		VALUE	VALUE (Ogirika <i>et al</i> ,2018)
1.	Flash point test(°C)	240	260- 280
2.	Viscosity(cSt)	32000	33000
3.	Fire Point(°C)	260	281
4.	Penetration Test(mm)	139.3	120
5.	Specific gravity	0.98	0.92-1.01
6.	Pour Point	42	44
7.	Softening Point Test(°C)	41	37
8.	API value	11.6	8.6- 11

Table 4.1 presents the physiochemical properties of the raw bitumen sourced from Agbavu in Ondo State, Nigeria.

The major properties investigated as shown in Table 4.1 includes viscosity test, API value, specific gravity, flash point test, pour point test, softening point test, penetration point and fire point test. When compared to values obtained from literature, the API gravity chart indicates that Nigeria bitumen with an API gravity of 11 is extra heavy in nature (smallley,2000)Other properties investigated followed the same trend as reported above. Results of bitumen obtained from Alaska. Canada, Venezuela, and Texas falls within the same range and can be classified as heavy oil or extra-heavy oil (Victor-Oji et al. 2017).

4.1.2 Catalyst characterization

The XRD pattern of equilibrated FCC catalyst and zeolite –Y are shown in Figure 4.1. The pattern shows that the peaks in zeolite-Y are also found in equilibrated catalyst which confirms that zeolite –Y is a major component of the FCC equilibrated catalyst. The crystallinity of Zeolite-Y is as presented in intensities of the reflection peaks at $2\theta = 7^\circ, 10.2^\circ, 18.7^\circ, 25^\circ$ and 31.5° (Jingjing et al., 2019). Which are also found in E-CAT, but the peaks are of smaller amount in the E-CAT than in zeolite- Y. This may be due to deposit of coke on the catalyst surface which reduced its activity.

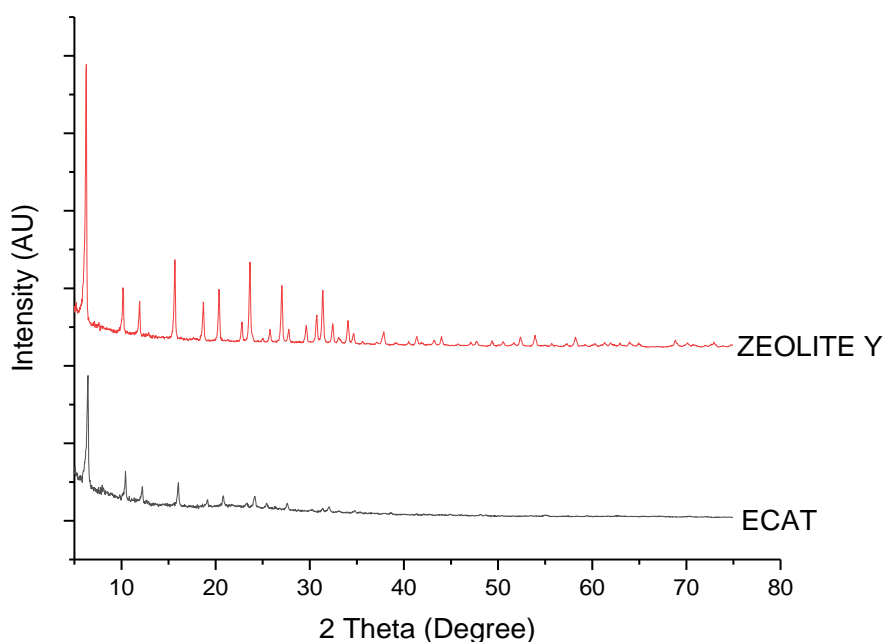


Figure 4.1 : XRD patterns of Zeolite-Y and E-CAT

The X-Ray Fluorescence (XRF) of the equilibrated catalyst is presented in Tables 4.2. It can be seen from the tables that the equilibrated catalyst contains the main oxides found in fresh zeolite –Y catalyst which includes SiO_2 , TiO_2 and Al_2O_3 among others, This is in agreement with results reported by Adeoye *et al*, 2017. However it can be seen that the percentage compositions of the elements and oxides are less in the E-CAT (about 40%) than the zeolite-Y. This is due to reduction in the activity of the equilibrated catalyst caused by deposit of coke in the surface of the catalyst and other factors. The XRF measurements further supplement the crystallography by providing spatial information on the quantification of oxides present in both catalysts. As previously suspected, oxides of phosphorus, chromium, manganese, zinc and strontium present in the E-CAT were the reason for lower intensity compared to zeolite Y as indicated in table 4.2. Sequentially, the Si/Al ratio of pure zeolite Y is higher than E-CAT as equally observed

by Hollander et al., 2002. The balance between zeolite –Y and E-CAT constitute of carbonaceous and volatile materials which was burned off or lost on ignition (LOI).

Table 4. 2: Elemental Composition of E-CAT and Zeolite-Y using X-Ray Floursence

OXIDE(%)	E-CAT	Zeolite-Y
Fe ₂ O ₃	0.582	1.42
MnO	0	0.11
Cr ₂ O ₃	0.045	0.099
TiO ₂	1.758	5.04
CaO	2.173	0.05
Al ₂ O ₃	12.378	31.30
MgO	0.555	0.666
ZnO	0.004	0.002
SiO ₂	27.48	58.5
K ₂ O	0.00	0.98
Si/Al ratio	2.22	1.86

FT-IR analysis of the catalyst was also conducted, result shows that the equilibrated catalyst has similar –OH functional group as the zeolite-y catalyst. Absorption in the regions of 900 to 1200 cm⁻¹ results from stretching and bending modes of Si-O or Al-O in framework in the zeolite-Y (Hossein *et al.*, 2013). The peaks at 3697, 3626 cm⁻¹ in spectra of zeolite-Y and 3362 cm⁻¹ in E-CAT correspond to O-H stretching (Hossein *et al.*, 2013; Ruiz-Baltazar *et al.*, 2015). The peak in the region of 1636 cm⁻¹ corresponds to O-H bending vibration for zeolite-Y but it's missing in E-CAT possibly due to reduced activity of the equilibrated catalyst caused by coke deposit on its surface. The cascaded result in Figure 4.2 showed that zeolite-y and E-CAT do not significantly differ from one another in the spectral regions 700 to 4000 cm⁻¹. This fact indicates that zeolite-y is a major component of E-CAT. This result agree with what

was reported by Adegoke *et al*,2016. It also agrees with what was reported in the XRD and XRF results.

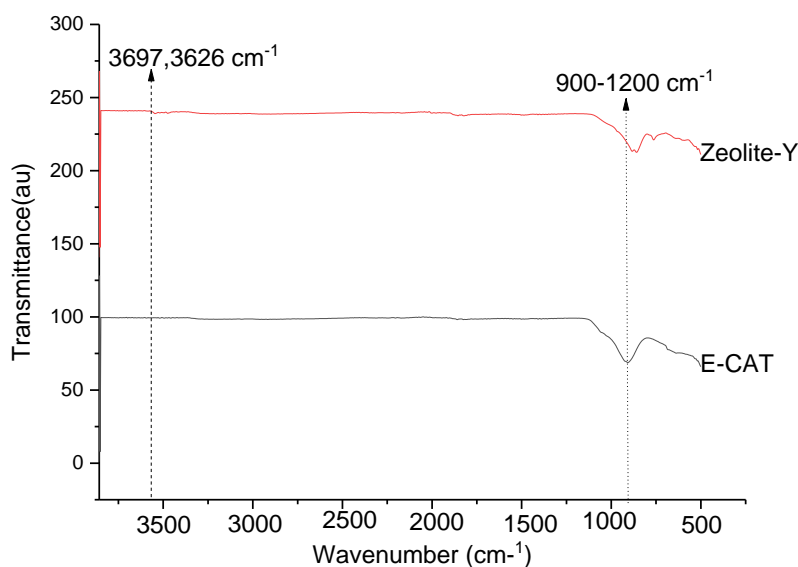


Figure 4. 2 : FT-IR spectra of zeolite-Y and E-CAT

4.2 Upgraded Model Oil Analyses

4.2.1 Viscosity analysis

Figures 4.3 present the viscosity results at different temperatures of vacuum gas oil (VGO) for both thermal and catalytic upgrading respectively. The results show that there was viscosity reduction after upgrading at all temperatures tested with higher percentage reduction recorded after catalyst addition. A 3.5, 10 and 37% reduction was recorded after thermal upgrade at 350, 400 and 450°C respectively as presented in Figure 4.3 while a higher reduction of 10, 15 and 42% was recorded after catalytic upgrade at temperatures of 350, 400 and 450°C correspondingly as presented in Figure 4.3. This reduction in viscosity is due to the conversion of heavy components of the VGO such as long chain saturated hydrocarbons and naphthenes to lighter components due to the activity of the catalyst and heat. The result agrees with what is reported by Meng *et*

al,2019 and Shuwa *et al*, 2017a both authors used VGO and heavy oil respectively in catalytic upgrading of heavy crude/bitumen with viscosity reduction achieved coupled with high yield of lighter distillates.

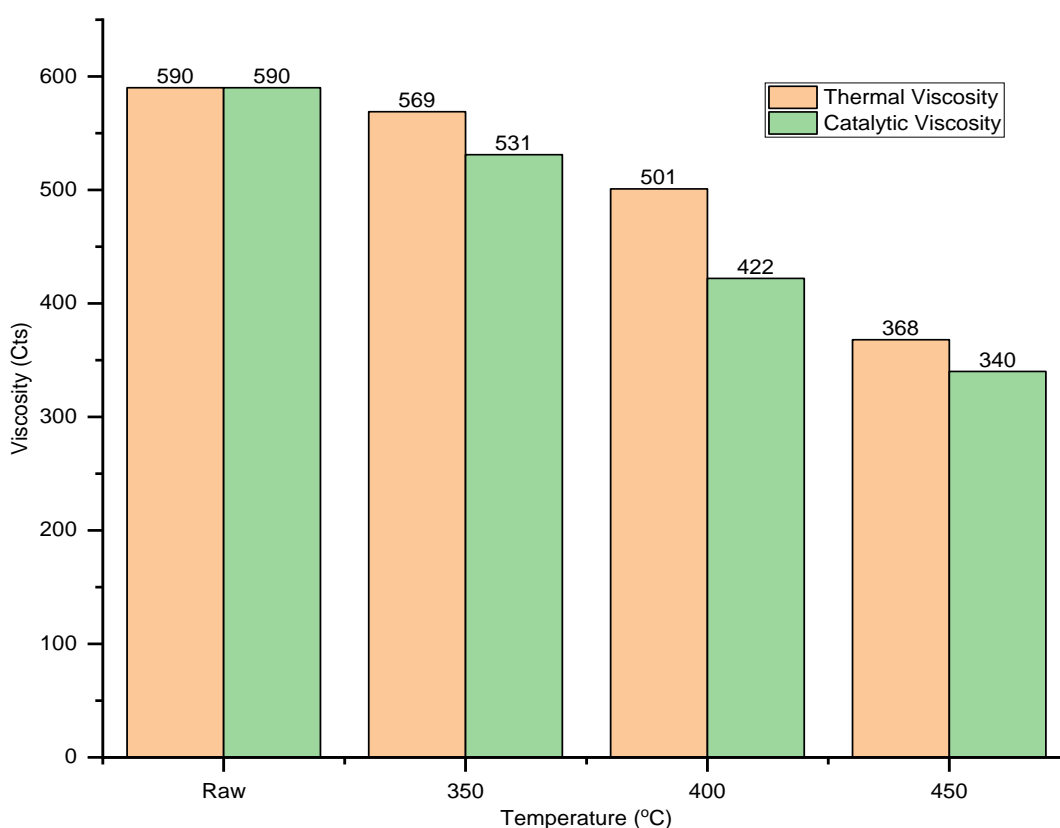


Figure 4.3: Viscosity values at different temperatures after thermal and catalytic upgrading of VGO

Figure 4.4 shows the FT-IR spectra of the raw and upgraded VGO at different temperatures. Results show the formation of more saturates with wavenumber 812cm^{-1} and 745cm^{-1} assigned to alkanes with C-H bond and bending vibration after upgrading reaction. There was also formation of aromatics at wavenumber 1714cm^{-1} and OH compounds were also formed.

The wave number 1457cm^{-1} and 1189cm^{-1} assigned C-H bending vibration of alkanes are seen after catalytic reaction. There were lighter compounds formed after catalytic reaction than in thermal reaction due to cleavage of bonds of large molecules by the action of catalyst and heat. The result agrees with what is reported by Meng *et al.*,2019 and Jingjing *et al.*,2019. Speculatively, cleavage of carbon-carbon bonds of the alkyl substituent in naphthenes, cleavage of the carbon-carbon bonds in high molecular weight long chain saturated hydrocarbons and ring openings of naphthenes could be responsible for the formation of lighter hydrocarbons. The catalyst active acidic sites present in the zeolite and the hydrogenation sites due to the present of metals are responsible for the reasons catalytic upgrading performed better than the thermal upgrade. The formation of lighter molecular compounds could be responsible for the viscosity reduction recorded as shown in Figures 4.3 .

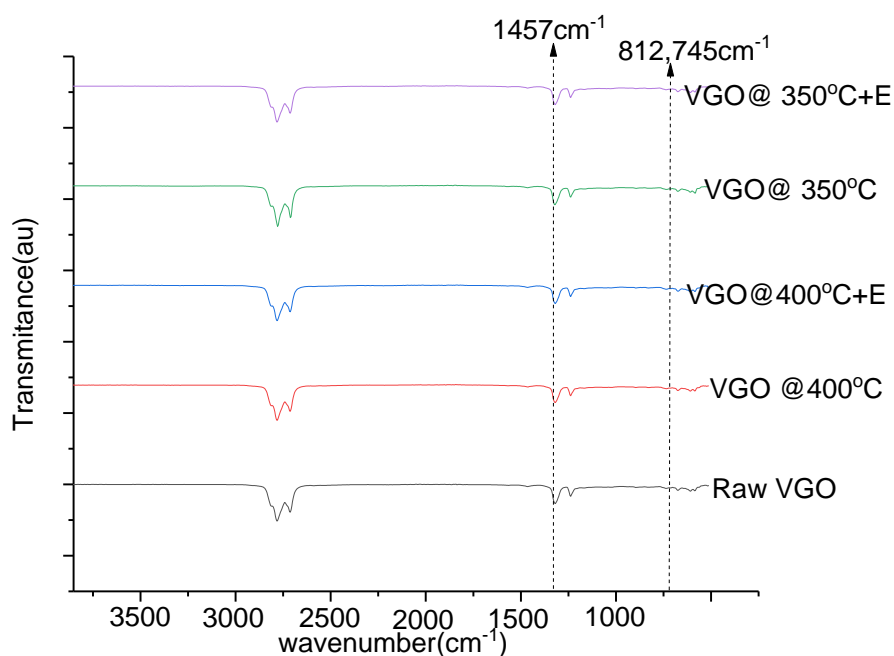


Figure 4.4: FTIR spectra of Raw VGO and upgraded VGO at different temperatures

Figures 4.5 present the viscosity result of heavy gas oil (HGO) upgrading. Viscosity decrease is observed from 350 to 450 °C with high percentage reduction recorded after catalytic reaction at each reported temperature. Again the decrease is much more in catalytic reaction than in thermal reaction. This agrees with what is reported by Jingjing *et al*, 2019. Specifically viscosity reduction of 4, 7 and 24% was recorded after thermal upgrade at 350, 400 and 450 °C respectively as shown in Figure 4.5 while 6, 13 and 33% viscosity reduction was recorded after catalytic reaction as can be seen in Figure 4.5. This shows a similar trend with VGO upgrading as discussed earlier. This agrees with the result reported by Onoriode *et al* in 2018.

Overall, the results showed that equilibrated catalyst played a significant role in the heavy oil upgrade.

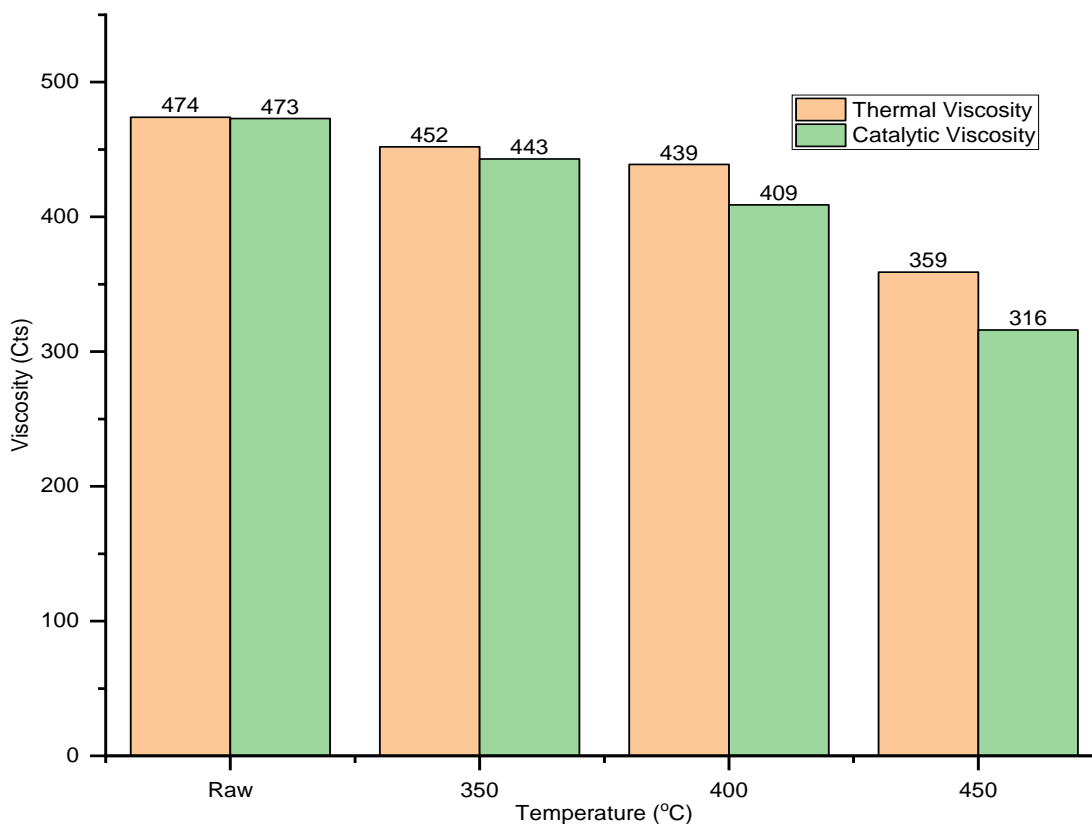


Figure 4.5: Viscosity values at different temperatures after thermal and catalytic upgrading of HGO

Figure 4.6 shows the FT-IR spectra of HGO at different temperatures, The wavenumber 2027.7 cm^{-1} assigned to heavy unsaturated molecule with $\text{N}=\text{C}=\text{C}$ in raw HGO was cracked by the action of heat and catalyst addition. A lighter compound with OH stretch with 1714 cm^{-1} can be seen in the upgraded oil. Another intermediate compound with wavenumber 961.7 cm^{-1} was formed after thermal reaction but was cracked during catalytic reaction. It can be observed that there was formation of alkane with wavenumber 812 cm^{-1} with C-H bond with bending vibration and O-H groups at 1185 cm^{-1} and 1714 cm^{-1} wave bands with stretching vibration. These showed the formations of more saturates and aromatics after catalytic reaction at different temperatures due to the presence of single bonds and $-\text{OH}$ group. This result agrees with what was reported by Onoriode *et al* in 2018. Similar observations were made with VGO upgrading using the catalysts (Jingjing *et al*,2019)

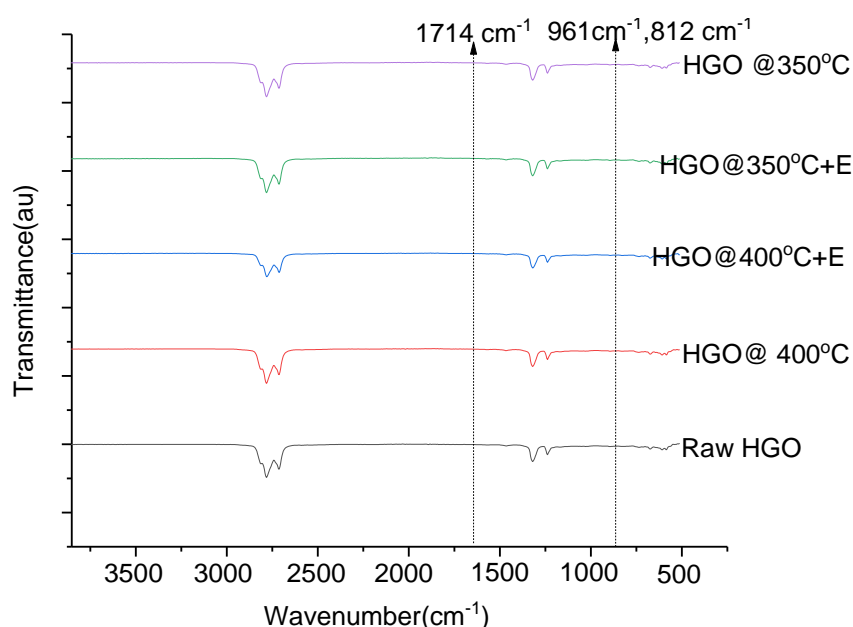


Figure 4.6: FTIR spectra of raw HGO and upgraded HGO at different temperatures

4.3 Upgraded bitumen analyses

4.3.1 Viscosity Analysis

The variation of bitumen viscosity before and after reaction is as shown in Table 4.3. The result from the table shows clearly that the viscosity was drastically reduced at higher temperature and by addition of catalyst. The viscosity reduction by thermal upgrade is 83 and 98% measured at room temperature and at 40°C respectively while the reduction after catalyst upgrade is 87.9 and 98.9% correspondingly. The result follows the same trend to what is reported by Onoriode *et al*,2018, in catalytic upgrade of bitumen in a hydrogen environment with viscosity reduction of 90.68% and also Jingjing *et al*,2019 with viscosity reduction of 81%.

Table 4.3: Viscosity variation of bitumen samples

Bitumen Samples/ Viscosity (cSt)	Temperature 25°C	Temperature 40°C
Raw Bitumen from Agbavu Ondo State	33,000	32,000
Viscosity (cSt)		
Thermally Upgraded bitumen at 350°C	5561	568
Viscosity (cSt)		
Catalytically upgraded bitumen at 350°C	4000	358
Viscosity (cSt)		

4.3.2: Physiochemical Analysis of upgraded bitumen

Table 4.4 presents the physical properties of the bitumen before and after upgrade. The result for raw bitumen analysis before upgrade follows the same trend with what is reported by Ogirikiet *al* 2018 and Guma et al ,2012. The results for upgraded bitumen shows that the viscosity of the bitumen at 40°C after thermal upgrade was 568cSt , specific gravity 0.895, fire point 200 ,flash point 230 and API gravity 26.6. This results shows that heat at temperature of 350°C has a significant impact on the upgrading of the bitumen. The results is as presented in column marked Thermal Value. The second set of values marked Catalytic value presents the values obtained after the catalyst reaction. The API gravity of 31, specific gravity of 0.8677, flash point of 180 and fire point of 230 shows that Nigeria bitumen was successfully upgraded to light oil with better result recorded after catalyst addition. The result of the upgraded oil follows the trend as reported by Abarasi Hart,2014 and Shuwa,et al,2017 with API gravity improvement. **Table 4.4: Physiochemical analysis of raw and upgraded bitumen**

S/N	Test	Value for Raw Bitumen	Thermal	Catalytic
1.	Flash point test (°C)	240	200	180
2.	Viscosity (cSt)	32000	568	358
3.	Fire Point (°C)	260	230	210
4.	Penetration Test (mm)	139.3	129	101
5.	Specific gravity	0.98	0.895	0.8677
6	API gravity	11.6	26.6	31
7.	Pour point	42	35	30

Table 4.5 presents the coke and asphaltene content of the bitumen before and after upgrading .Result shows decrease in quantity of coke formed from thermal to catalytic

reaction, also the asphaltene content was found to have reduced after upgrading reaction. This can be as a result cleavage of C-S, C-S, C-H bonds in the heavy oil, Zhenyu Tang, 2019. This result also agrees with what is reported by Maldonado *et al.*, 2018 and Abdullahi *et al.* 2016

Table 4.5: Coke and asphaltene content of raw and upgraded bitumen

	Coke(mg)	Asphaltene (mg)
Raw	0.0	170
Thermal	0.21	70
Catalytic	0.1	50

4.3.3 FT-IR Analysis

The FT-IR spectrum of bitumen before and after upgrading were used to analyse the variation of structures from the view of molecules as shown in Figure 4.8. The peak 697cm^{-1} assigned to C-S bond with stretching vibration in the bitumen was weakened after the upgrading reaction. Notably, the extent to which the C-S bond was broken in the heavy oil after catalytic upgrading reaction was greater than that of heavy oil after thermal upgrade. Besides the peak at 2855.1cm^{-1} and 2922.2cm^{-1} assigned to methylene with stretching vibration were weaker in the bitumen after the reaction (Jingling *et al.*, 2019). This implies that dealkylation went on during the upgrading process. The peaks 3619.2cm^{-1} and 3697.2cm^{-1} with stretching vibration assigned to large OH molecular compounds in the raw bitumen were missing in the upgraded ones while lighter compounds has been formed indicating the conversion of the bitumen to

light oil. The peak 3399.3cm^{-1} which represents aliphatic amine and 2139.8cm^{-1} and 2072.4cm^{-1} assigned to unsaturated alkenes with asymmetric stretch were also broken down. Notably the peak 1208.7cm^{-1} with stretching vibration assigned to sulphur compound has been eliminated which confirms the cracking of resins and asphaltene compounds which accounts for the heaviness in the bitumen.

Finally the major difference between the thermal and catalytic upgraded bitumen is the compound $\text{N}=\text{C}=\text{S}$ with peak number 2072.4 which represents unsaturated nitrate compound found in the thermally upgraded oil but absent after catalytic upgrade.

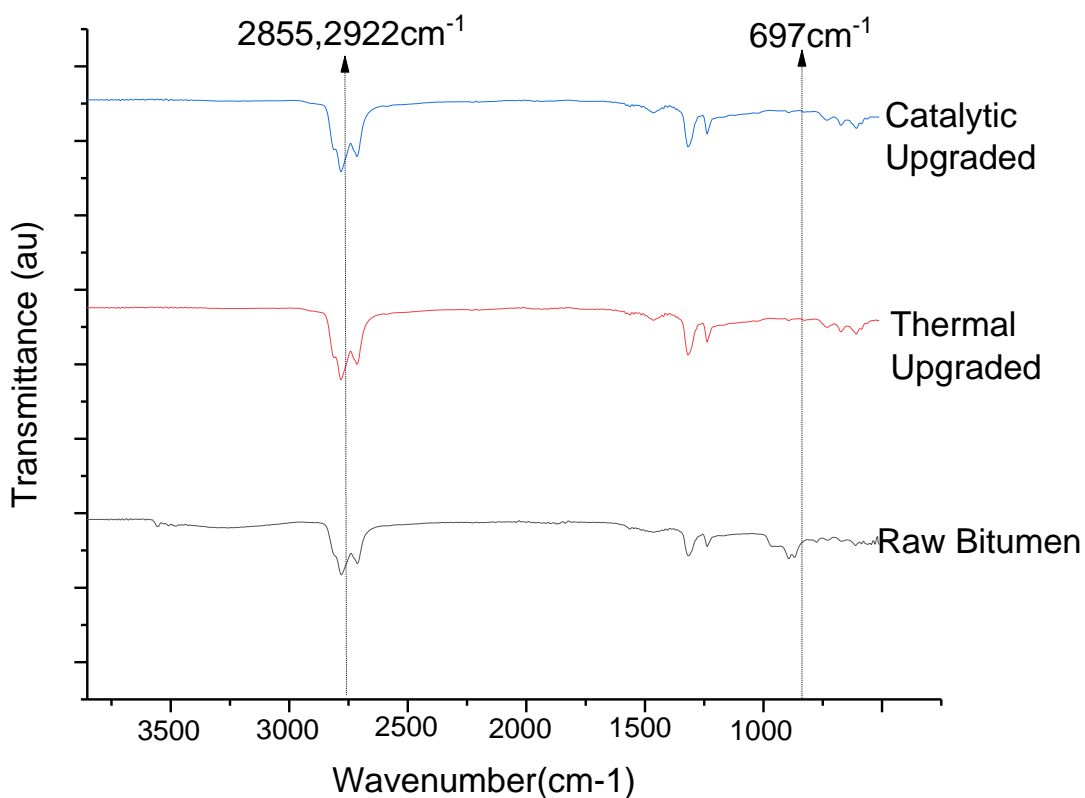


Figure 4.8: FT-IR spectra of raw and upgraded bitumen

4.3.4: GC-MS analysis

In order to elucidate the extent of upgrading in a bid to analyze the types of components formed during cracking, GC-MS analysis was performed on the fresh bitumen, thermally cracked bitumen and catalytic upgraded bitumen as reported in Tables 4.6-4.8. Results show that the fresh bitumen contains heavy heteroatoms (N and O) and acidic compounds (Smith et al., 2008) with Si from clay particles identical of typical oilsand bitumen. Conversely, after upgrading pure aromatic compounds were formed with combined 12.02 wt% for thermal cracking and 17.8 wt% during catalytic upgrading. It is pertinent to state here that the GC method employed elutes both pure aromatic and polar aromatic compounds up to unsaturated compounds (Onoriode et al., 2020).

Table 4.6: GC-MS analysis of fresh bitumen

Ret. time	Weight % m	Rel. area %	Nomenclature	Mol. formula
5.01	2.74	4.22	Cyclopentane,1,3-dimethyl – cis	C ₉ H ₁₄
6.42	6.43	6.09	Hexane,3-methyl-	C ₇ H ₁₆
7.92	0.86	6.60	Acetic acid chloroethyl ester	C ₄ H ₇ ClO ₂
9.34	0.11	7.65	1,4,Bistrimethylsilyl benzene	C ₁₂ H ₂₂ Si ₂
10.68	0.88	8.71	Oxirane,hexadecyl	C ₁₈ H ₃₆ O
11.93	7.68	9.76	n-nexadexanoic acid	C ₁₆ H ₃₂ O ₂
14.26	9.76	14.25	Tetrasiloxane decamethyl	C ₁₀ H ₃₀ O ₃ Si
15.31	21.01	8.41	Oleic acid	C ₁₈ H ₃₂ O ₂
16.26	8.0	8.81	Octadenoic acid	C ₁₈ H ₃₆ O ₂
17.18	3.42	7.65	Cylobabitol	C ₁₂ H ₁₀ N ₂ O ₃
18.06	1.92	6.33	2-Octantal	C ₈ H ₁₄ O
18.98	0.93	5.81	4-chlor-2,4dimethylhexane	C ₈ H ₁₇ Cl
19.72	1.0	4.75	Tetradecanoic acid	C ₁₄ H ₂₈ O ₂
22.0	0.30	0.50	Dedecanoic acid	C ₁₂ H ₂₄ O ₂
28.96	0.30	0.26	1- Octadecaene	C ₁₈ H ₃₆

Table 4.7: GC-MS analysis of thermally cracked bitumen

Ret. time	Weight % m	Rel. area %	Nomenclature	Mol. formula
4.96	5.77	6.25	Toluene	C ₇ H ₈
6.29	4.41	3.61	Benzene	C ₆ H ₆
7.82	1.84	1.80	Styrene	C ₈ H ₈
9.31	3.42	1.08	Butanol 2,2 dimethyl	C ₆ H ₁₄
9.70	3.41	1.68	3,5-Dimethoxycinnamic acid	C ₁₁ H ₁₂ O ₈
11.80	3.40	2.89	1-butane 1- phynol	C ₁₀ H ₁₂ O
11.92	1.99	1.68	1-heptene	C ₇ H ₁₄
14.26	7.11	1.68	Octan- 4-ethyl	C ₁₀ H ₂₂
15.24	2.98	2.16	Undecane	C ₁₁ H ₂₄
16.61	2.98	2.28	4-Hydroxy-2-methoxycinnamaldehyde	C ₁₀ H ₁₀ O ₃
16.79	2.01	4.89	Pyridine	C ₅ H ₅ N
17.11	7.13	3.37	2,5- dimethyl furan	C ₆ H ₈ O
17.97	4.27	3.31	Cyclopentanone,2-methyl	C ₆ H ₁₀ O
19.00	11.57	4.33	Phenol	C ₆ H ₆ O
19.96	6.41	5.05	1,2-Benzenedicarboxylic acid	C ₈ H ₆ O ₄
20.32	3.93	8.17	Phenol, 2,3,6-trimethyl-	C ₉ H ₁₂ O
21.10	0.18	8.89	Aniline	C ₆ H ₇ N
21.98	12.71	12.02	n- Hexadecanoic acid	C ₁₆ H ₃₂ O ₂

Table 4.8:GC-MS analysis of catalytic upgraded bitumen

Ret. time	Weight % m	Rel. area %	Nomenclature	Mol. formula
5.00	7.77	3.30	Benzene	C ₇ H ₆
6.42	3.02	4.61	Toulene	C ₇ H ₈
7.42	1.44	1.02	Styrene	C ₈ H ₈
7.92	2.81	5.22	o-xylene	C ₈ H ₁₀
9.34	2.29	2.29	n-propyl benzene	C ₉ H ₁₄
9.98	2.76	6.04	1-butanol -1phenol	C ₁₀ H ₁₂ O
10.26	2.0	1.43	Naphthalene,1,6-dimethyl-	C ₁₂ H ₁₂
10.68	7.11	6.61	Phenanthrene	C ₁₄ H ₁₀
11.31	0.98	4.19	9,10-dihydroanthracene	C ₁₄ H ₁₂
11.98	2.59	7.45	p- cresol	C ₁₀ H ₅ O
12.84	2.01	2.10	1- naphthol	C ₁₈ H ₁₂
13.28	7.13	7.34	Chrysene	C ₁₀ H ₁₂ O ₂
13.34	2.11	2.84	Isoeugenol	C ₁₀ H ₁₂ O ₂
14.26	5.96	7.24	Phenol	C ₆ H ₆ O
15.30	7.15	6.61	1,2-Benzenedicarboxylic acid	C ₈ H ₆ O ₄
16.32	6.77	6.50	Phenol, 2,3,6-trimethyl-	C ₉ H ₁₂ O
17.21	7.54	6.08	Aniline	C ₆ H ₇ N
18.66	12.90	5.35	n- Hexadecanoic acid	C ₁₆ H ₃₂ O ₂
18.98	4.43	4.51	Diethyl phthalate	C ₁₂ H ₁₄ O ₄
19.74	2.61	3.81	3,5-Dimethoxycinnamic acid	C ₁₁ H ₁₂ O ₄

Consequently; phynol, phenol and 2,5 – dimethyl furan were classified as unsaturated compounds. With this classification, unsaturates formed weighed a combined 26.03 wt% for thermal cracking and 18.08 wt% for catalytic upgrading. This result summarized the effect of the E-CAT in cracking asphaltene to more aromatics and less unsaturated hydrocarbons.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

From the research work done, the following conclusion can be drawn:

- (i) Nigeria bitumen /oil sand was sourced from Agbabu in Ondo state and characterized. Result showed API gravity of 11, viscosity of 32000cSt, specific gravity of 0.98 and pour point of 42 which are typical of extra heavy oil.
- (ii) An FCC equilibrated catalyst (E-CAT) was sourced from Kaduna Refining and Petrochemical Company Ltd (KRPC) and characterized. Initial characterization study showed it contains active constituents required of a commercial FCC catalyst. The XRD result showed the reflection peaks at $2\theta = 7^\circ, 10.2^\circ, 18.7^\circ, 25^\circ$ present in zeolite-Y are also found in E-CAT though in smaller amount, XRF result showed both contains similar oxides like Al_2O_3, SiO_3 but the percentage composition is lower in E-CAT due to reduction in activity caused by coke deposits. FT-IR result followed the same pattern as reported above
- (iii) Upgrading of HGO and VGO used as model oil was undertaken using equilibrated FCC catalyst. Results of VGO upgrade showed viscosity reduction of 3.5, 10 and 32% after thermal upgrade at 350,400, 450°C and 10, 15 and 42% after catalyst addition at the same temperatures. The HGO upgrading result showed viscosity reduction of 4, 7 and 24% after thermal upgrade at 350,400 and 450°C respectively and 6,13 and 33% viscosity reduction after catalyst addition correspondingly. FT-IR results suggest the formation of saturated hydrocarbons an indication of the formation of valuable products after upgrading reactions with a better results recorded after catalyst addition.

- (iv) In the presence of an FCC equilibrated catalyst and a hydrogen source, the raw bitumen was heated to 350°C at a pressure of 10bar. The reaction went on for two hours after attaining the set temperature of 350°C before the reactor was automatically switched off. Result of product analysis shows that viscosity reduction by thermal upgrade were 83% and 98 at room temperature and at 40°C respectively while the viscosity reduction after catalyst reaction were 87.9% and 98.9 at room temperature and at 40°C correspondingly. API gravity and other properties of the bitumen before and after the upgrade like pour point, penetration point, specific gravity, and fire point were also investigated. Result shows that there were significant improvement towards the formation of light oil. The FT-IR and GC-MS results shows that the heavy components of the bitumen like resins and asphaltene were drastically reduced hence the successful upgrading of the bitumen using equilibrated catalyst

5.2 Recommendations

The following recommendations were given for this research work:

- (i) Researchers should explore more sources of hydrogen like biomass in future research work
- (ii) Other zeolite type like ZSM-5 should be used for the upgrading reaction and result compared with equilibrated catalyst
- (iii) The gases produced during reaction and the catalyst should be recovered and analysed for further insight

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APPENDICES

Appendix A : Calculation on density determination for bitumen

$$\text{Density: } 18^{\circ}\text{C } \frac{\text{Mass}}{\text{Volume}}$$

$$\text{Thermal: } \frac{66.12-29.84}{40} = \frac{36.264}{40} = 0.9066\text{mg/l}$$

$$\text{Catalytic Upgraded: } \frac{72.15-30.84}{47} = \frac{41.31}{47} = 0.879\text{mg/l}$$

$$\text{Water: } \frac{41.07-30.94}{10} = \frac{10.13}{10} = 1.013\text{mg/l}$$

$$\text{Specific gravity (18}^{\circ}\text{c)} \frac{\text{Density of substnce}}{\text{Density of equal of water}}$$

$$\text{Thermal: } \frac{0.90660}{1.013} = 0.895$$

$$\text{Catalytic Upgraded: } \frac{0.879}{1.013} = 0.8677$$

Appendix B: Determination of API gravity

$$\text{API} = 141.5/\text{SG} - 131.5$$

$$\text{For thermally upgraded oil} = \frac{141.5}{\text{SG}} - 131.5$$

$$= \frac{141.5}{0.895} - 131.5 = 26.60$$

$$\text{For catalytically upgraded bitumen} = \frac{141.5}{\text{SG}} - 131.5$$

$$= \frac{141.5}{0.866} - 131.5 = 31$$

Appendix C : Viscosity test for bitumen

Thermal cracking

Speed = 30rpm

$\gamma = 20,00\text{mp}$

Room Temperature

Angle 20.9

Viscosity=4000mpa

Temperature of 40⁰c

Angle: 21.82

Viscosity: 568mpa

Catalytic cracking

Room temperature

Speed= 30rpm

Angle: 29.1

Viscosity: 5561mpa

Temperature of 40⁰C

Viscosity =358mpa

Appendix D: Determination of coke content of the upgraded oil

Weight of Empty Container: 8.90g

Weight of container + oil = 8.45g

Bitumen = 1g

Volume of TCM = 40ml

Coke determination for thermal upgraded oil

Weight of filter paper = 0.77g

Weight of filter paper + coke = 0.98g

Weight of coke = 0.21g

Coke determination for catalytic Upgraded oil

Weight of filter paper = 0.77g

Weight of filter paper + coke = 0.888g

Weight of coke = $0.77 - 0.888 = 0.1$ g

Appendix E : Determination of asphaltene content of oil

Weight of container = 7.95g

Weight of container + oil = 8.45g

Weight of Oil = 500mg

Volume of n – hexane = 40ml

Weight of container + oil after 24 hours = 8.5g

Mass of Asphaltene precipitate = 0.05g = 50mg = 10w%,