DEVELOPMENT OF Pt-Zn/Al_2O_3 CATALYST FOR n-OCTANE REFORMING

By

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By

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DECLARATION

I, Oloworishe Femi John, hereby declare that the work in this thesis titled “Development of Pt-Zn/Al_2O_3 Catalyst for n-octane reforming” was performed by me in the Department of Chemical Engineering, Ahmadu Bello University, Zaria, under the supervision of Prof. B. O. Aderemi, Dr. A. Atta, and Dr. B. Mukhtar.

All information derived from literature have been duly acknowledged and a list of reference provided. No part of this work has been presented for another degree or diploma at any institution.

………………………… ……………………….

Signature Date

CERTIFICATION

This thesis titled “Development of Pt-Zn/Al_2O_3 Catalyst for n-Octane reforming” meets the regulations governing the award of the degree of Master of Science (MSc.) of the Ahmadu Bello University Zaria, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

I dedicate this project work to God Almighty, and to Jesus Christ our Lord and Savior.

ACKNOWLEDGEMENTS

I sincerely appreciate the divine privilege granted me by God to embark on this project. To HIM alone be all the glory. My parents labored tirelessly in enhancing my career prospect; I remain grateful for such an upbringing. Indeed, they remain an icon to me even in their memorial. Adieu! The supports of my wife (Gloria) and my precious daughter (Molayo) are immensely appreciated.

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ABSTRACT

Six different platinum and zinc gamma-alumina supported catalysts were developed by impregnation method. Five of the catalysts consist of 1.0% wt of Zn and varying amounts of Pt (0, 0.5, 1.0, 1.5, 2.0% wt) while the sixth catalyst was chlorinated gamma-alumina, having no active metal(s) serving as the control sample. The catalysts were characterized using X-ray diffractometer (XRD), Brunauer-Emmett-Teller (BET), and scanning electron microscope (SEM) techniques. The catalytic performances of these catalysts were evaluated with respect to n-octane reforming in a packed tubular reactor. The XRD patterns show that the chlorinated support (γ-Al_2O_3) is amorphous as its diffractograph was characterized by low intensity counts and broad peaks. The other catalysts had similar Bragg angles. The textural properties determined by the BET analyses were: specific surface area ranging from $44m^2/g$ to $78m^2/g$, pore volume ranging from $0.02cm^3/g$ to $0.04cm^3/g$, and pore size ranging from 2.00nm to 2.10nm. The catalytic performances of the catalysts for n-octane reforming were determined at varying reactor temperatures (430^0C, 455^0C, 480^0C, 505^0C, and 530^0C). The results showed low reformate yield at low reactor-temperatures (430-455^0C) when the reactor was packed with the chlorinated gamma-alumina. Nonetheless, a significant improvement in the reformate yield was observed at higher temperatures ($T \geq 455^0C$). When the Zn/Al_2O catalyst was used, the reformate yield increases from a minimum of 46% at 430^0C to a maximum of 83% at 530^0C. The set of four Pt-Zn/Al_2O_3 catalysts (with 0.5, 1.0, 1.5, 2.0%wt Pt) showed similar trends in reformate yields with changes in temperature, showing minimum yield of about 25% at 430^0C and maximum yield of 84% at 480^0C. Beyond this point (480^0C), the yields pattern became erratic. The selectivity of all the catalysts for aromatics were quite impressive. The chlorinated support had high selectivity for iso-paraffins, while the metal dispersed catalysts favor formation of

aromatics. Technically, the 1.5%wt Pt-Zn/Al_2O_3 catalyst demonstrated the best performance, but economic consideration may support preference for 0.5%wt Pt-Zn/Al_2O_3 catalyst.

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ABBREVIATIONS AND SYMBOLS

ABU	Ahmadu Bello University, Zaria
. . . *et al*	. . . “and others”
API	American Petroleum Institute
BET	Brunauer-Emmett-Teller
cm	centimeter
^{0}C	degree Celsius; (unit of temperature)
θ	Diffraction angle (^{0})
FCCU	Fluid catalytic cracking unit
Hr	hour(s)
C_6, C_7, C_9, C_{10},	hexane, heptanes, nonane, decane; (paraffinic hydrocarbons)
GC-MS	Gas chromatograph mass spectrophotometer
G	gram
in	inch
ICEs	internal combustion engines
kg	kilogram
kPa	kilopascal
m	metres
µm	micrometer
ml	milliletres
MLPD	million liters per day; (1barrel ≈ 158 liters)
ML^{-1}	mole per litre
nm	nanometer

NARICT	National Research Institute for Chemical Technology, (in Zaria)
NGRC	National Geological Research Centre, Kaduna
n-octane	normal octane
PPM	parts per million
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
SSA	Specific surface area per unit mass; (m^2/g)
UOP	Universal oil products
wt%	weight percent
XRD	X-ray diffraction

CHAPTER ONE

INTRODUCTION

1.1 PREAMBLE

Gasoline is a complex mixture of relatively volatile hydrocarbons with or without small quantities of additives, blended to form a fuel suitable for use in internal combustion engines (ICEs). The ICEs became a far better alternative to the steam propelled engines, used in the antiquity, which are often bulky and relatively inconvenient. Gasoline consumptions have increased globally since the advent of modern civilization, and the revolutionary growth in automobile industries. In 2010 alone, the global consumption stood at about 3498million litres per day (MLPD). Annually, the consumption increased by about 37MLPD, while local consumption rate within Nigeria stood at about 31MLPD; valued at about 3billion Naira, (IES, 2013).

Gasoline is produced by blending several gasoline components, such as reformate (reformed naphtha), FCC gasoline, alkylate, and others. Catalytic reforming of heavy naphtha constitutes a very important source of products having high octane numbers which are key components in the production of gasoline. Catalytic reforming is the process of transforming hydrocarbons with low octane numbers to aromatics and iso-paraffins which have high octane numbers. The catalytic reformer is one of the major units for gasoline production in the refineries. It can produce 37 wt% of the total gasoline pool, while about 50% of the pool may come from the fluid catalytic cracker (FCC), (Kjell *et al* 2004). Other gasoline producing units are: alkylation and isomerization.

The octane number of gasoline is a measure of its resistance to knock and is determined by comparing the characteristics of a gasoline to those of isooctane (2,2,4-trimethylpentane) and heptanes. Isooctane is assigned an octane number of 100. It is a highly branched compound that burns smoothly, with little or no knock. On the other hand, heptanes, a straight chain, unbranched molecule is given an octane rating of zero because of its poor knocking properties, (Carl 2013).

A major defect with the straight-run gasoline, SRG, (obtained directly from the distillation column) is the low octane number (about 70%), and presences of certain impurities, thus making it unfit for use in most automobiles. The FCC gasoline may contains over 10ppm of sulphur compounds or mercaptans, hence, the need for subsequent hydrodesulfurization; which results to reduction or decline in octane number. Such treatments may reduce the octane number to about 86.5%, whereas gasoline for internal combustion engines is expected to have an octane rating of at least 90%, Kjell *et al* (2004). Thus, regardless of the availability of FCC gasoline, the gasoline pool is largely dependent on the reformate from the catalytic reforming unit which serves as octane number moderator. Thus, making reformate the most vital component for gasoline blending.

In the past decades, use of several octane number boosters or additives had been attempted, but not without their adverse health and environmental consequences. Such additives include methyltertbutyl ether (MTBE), ethyltertbutyl ether (ETBE), isooctane, toluene and tetraethyl lead (TEL). Nigerian refineries, were in the 1980s making use of TEL to boost the quality of her gasoline, but had since phased-out such practices. Advancement in the catalytic reforming unit (CRU) technology for reformate production has provided global solution to the gasoline's octane number challenges (George *et al*, 1996).

Modern reforming catalysts in use today contain platinum supported on silica, silica-aluminum, or alumina base. In most cases, rhenium (Re) is combined with platinum to form a more stable catalyst that permits operation at lower pressures. Platinum is thought to serve as the catalytic site for hydrogenation and dehydrogenation reactions. Chlorinated alumina provides the acidic site for isomerization, cyclization, and hydrocracking reactions. Reforming catalyst activity is a function of surface area, pore volume, and active platinum and chlorine content (George and Abdullahi, 2005).

Naphtha is a mixture of many different hydrocarbon compounds. It has an initial boiling point of about 35^oC and a final boiling point of about 200^oC, and it contains paraffin, naphthene (cyclic paraffins) and aromatic hydrocarbons ranging from those containing four to those containing about eleven carbon atoms. Naphtha is a highly volatile product obtained from crude oil by direct atmospheric distillation and by catalytic cracking of heavy residues. The naphtha derived from the distillation of crude oils is referred to as ‘straight-run’ naphtha. Straight-run naphtha are often further distilled to produce a light naphtha containing mainly of the hydrocarbons with six or less carbon atoms and a heavy naphtha containing mainly of the hydrocarbons with more than six carbon atoms. The heavy naphtha, which has an initial boiling point of about 70^oC and a final boiling point of about 190^oC, served as feed to a catalytic reformer (OSHA, 2005). For instance, n-octane (C_8H_{18}) has 8 carbon atoms and a boiling point of $125\text{-}127^0C$.

Catalytic reforming is a process whereby heavy naphthas are contacted with a platinum-containing catalyst at elevated temperatures and hydrogen pressures ranging from 345 to 3,450 kPa for the purpose of raising the octane number of the hydrocarbon feed stream. The low octane, paraffin-rich naphtha feed is converted to a high-octane liquid product that is rich in aromatic compounds. Reformate is the focal end-product of this process. However, hydrogen and liquified petroleum gases (LPG) are also produced as reaction by-products. In addition to the use of reformate as a blending component of motor fuels (gasoline), it is also a primary source of aromatics used in petrochemical industry (Huebner, 1999).

1.2 RESEARCH PROBLEM

Pt/Al_2O_3 catalyst is widely used in CRU reforming processes. However, the cost of Pt poses economic challenges to its uses. The incorporation of Zn to supplement the Pt (as in $Pt\text{-}Zn/Al_2O_3$ catalyst) can be a cost saving approach. Thus, the need to ascertained the viability of $Pt\text{-}Zn/Al_2O_3$ catalyst for reforming process.

1.3 AIM AND OBJECTIVES

1.3.1 Aim

The study is aimed at preparing $Pt\text{-}Zn/Al_2O_3$ catalysts (with varying platinum loading) and testing the prepared catalysts for reforming capability using n-octane as a representative substrate.

1.3.2 Objectives

1. To prepare a Zn/Al_2O_3 and set of $Pt\text{-}Zn/Al_2O_3$ catalysts
2. To characterize the prepared catalysts
3. To test the effectiveness of the developed catalysts in a model reforming process

1.4 SCOPE OF WORK

1.4.1 Catalysts Preparation

1. Preparation of a monometallic catalyst (Zn/Al_2O_3)
2. Preparation of bimetallic catalysts ($Pt\text{-}Zn/Al_2O_3$)

1.4.2 Characterization Experiments

The prepared catalysts will be characterized to determine their:

1. Crystal structure
2. Degree of metal dispersion
3. Specific surface area
4. Pore volume

1.4.3 Reforming and Analyses

1. Analysis of the feed (n-octane)
2. Reformation of the feed using the prepared catalysts
3. Analysis of the reformate samples

1.5 JUSTIFICATION

1. Zn is more readily available and far cheaper than Pt, thus, the use of Pt-Zn/Al_2O_3 catalyst in place of Pt/Al_2O_3 catalyst for reforming processes can be a cost-reduction approach.
2. The research will boost the indigenous understanding of catalyst preparation technologies.
3. The catalyst support was sourced locally from Kankara Kaolin Clay, thus guaranteeing cost reduction in the catalyst development.

CHAPTER TWO

LITERATURE REVIEW

2.1 CATALYSTS AND CATALYSIS

A catalyst is a chemical substance that affects the rate of a chemical reaction by altering the activation energy required for the reaction to proceed. Catalysts permit an alternate mechanism for the reactants to become products, with a lower activation energy and different transition state. A catalyst may allow a reaction to proceed at a lower temperature or increase the reaction rate or selectivity. Catalysts often react with reactants to form intermediates that eventually yield the same reaction products and regenerate the catalyst. The catalyst may be consumed during one of the intermediate steps, but it will be regenerated before the reaction is completed (Anne, 1999). The surface structure of a catalyst is an important feature because that is where the reaction takes place (Jackson, 2011).

The process whereby the rate is altered (increased or decreased) using a catalyst is called catalysis (Ronald *et al*, 1999). Likewise, Fogler (2006) defined catalysis as the occurrence, study, and use of catalysts and catalytic processes. A catalyst is not consumed by the reaction and it may participate in multiple reactions at a time. The basic difference between a catalyzed reaction and an uncatalyzed reaction is that the activation energy is different. There is no effect on the energy of the reactants or the products. Figure 2.1 shows an uncatalyzed reaction path in comparison with a catalyzed reaction. It is obvious that the catalyzed reaction has lower activation energy.

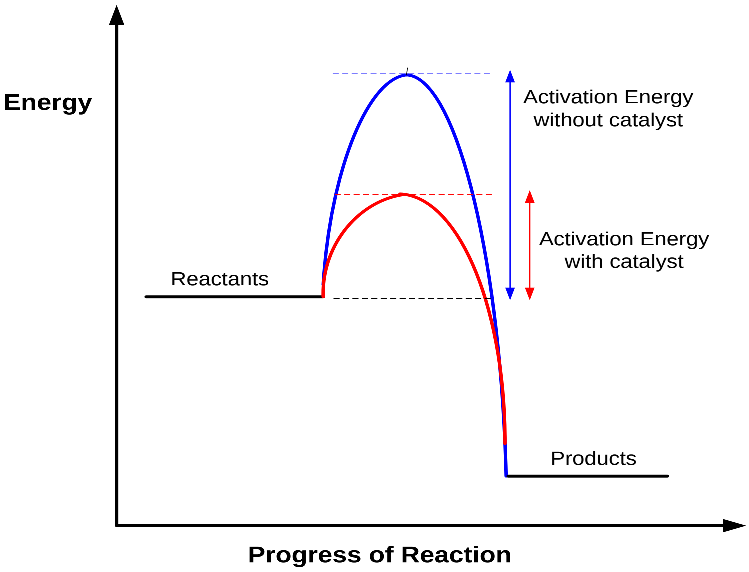


Figure 2.1: Effects of catalyst on activation energy, (www.chemguide.co.uk, 2011).

Ronald *et al* (1999) identified the following types of catalysis: molecular catalysis, surface catalysis, enzyme catalysis, autocatalysis, homogeneous catalysis, and heterogeneous catalysis.

2.1.1 Properties of a Good Catalyst

A catalyst has several properties that include:

i. It speeds the reaction. i.e. it increases the rate of a reaction
ii. It is not consumed in the reaction.
iii. It helps bring the reactants together in the correct orientation
iv. It provides a surface on which the reaction occurs.
v. It provides an alternative pathway (of lower activation energy)
vi. Catalyst cannot make impossible reaction to occur and does not initiate a reaction. (Ronald *et al*, 1999).

2.1.2 History of Catalysis

In a general sense, anything that increases the rate of a process is a "catalyst", a term derived from Greek καταλύειν, meaning "to annul", or "to untie", or "to pick up". The phrase *catalyse processes* was coined by Jöns Jakob Berzelius in 1836 (Keith and Meiser, 1982) to describe reactions that are accelerated by substances that remain unchanged after the reaction. Other early chemists involved in catalysis were Alexander Mitscherlich who referred to contact processes and Johann Wolfgang Döbereiner who spoke of contact action and whose fire lighter based on hydrogen and a platinum sponge became a huge commercial success in the 1820s. Humphry Davy discovered the use of platinum in catalysis. In 1885, Wilhelm Ostwald at Leipzig University started a systematic investigation into reactions that were catalyzed by the presence of acids and bases, and found that chemical reactions occur at finite rates and that these rates can be used to determine the strengths of acids and bases (Roberts, 2000). One current area of active research in catalysis is that of enzymes. Natural enzymes have long been used by a few industries, but fewer than 20 such enzymes are presently available in industrial amounts.

Catalysis has played a central role in the chemical industry from its beginning in the late eighteenth century. Today, catalytic processes are used to make gasoline, to synthesize most pharmaceuticals, chemicals, polymers, and to reduce pollution from cars and power plants. The discovery of new catalysts create new product, such as polypropylene, or dramatically improves the manufacture of existing ones, such as gasoline. In the first decades of the nineteenth century, scientists, including Michael Faraday, investigated chemical reactions initiated by platinum. In 1836, Berzellus coined the word catalysis to generalize a growing body of experimental data. Half century later, Wilhelm Ostwald linked catalysis to chemical thermodynamics and kinetics by defining catalysts as substances that alter the velocity of chemical reactions without appearing in the end products. About the same time, many chemists were using heterogeneous catalysts to develop new processes, the most significant of which was the Haber, Bosch, and Mittasch ammonia processes. The dramatic success of the chemical industry throughout most of the twentieth century in no small part was made possible by discovery of new catalysts. Given the growing importance of catalysis to the chemical industry, many researchers investigated the fundamental mechanisms of catalysis. While many specific advances were made, no general theory emerged. Since the 1960s, academic research in catalysis has used increasingly sophisticated analytical techniques to explore catalytic phenomena at the atomic level. In part, due to the maturity of chemical industry, this new knowledge has been converted into major new catalytic technologies, (Smith, 2010).

2.1.3 Classification of Catalysts

(i) Positive and Negative Catalysts

A catalyst which increases the rate of a chemical reaction is called positive catalyst. Such catalyst decreases the activation energy by accepting a smaller reaction path, so the rate of reaction rate is increased. A catalyst which decreases or retards the rate of reaction is called negative catalyst.

(ii) Heterogeneous and Homogenous Catalysts

Jackson (2011) described heterogeneous catalysis as the use of catalysts which are in a different phase from the reactants. He stressed that in heterogeneous catalysis, when the reactants, which are usually in gaseous or liquid phases, flow through a reactor and sorb onto the surface of a solid catalyst, a reaction takes place, and then the products desorb. The reactants are taken downstream for further use, and the catalyst remains unchanged in the process. Heterogeneous catalysis favour most industrial processes.

In homogeneous catalysis, the reactants and the catalyst are in the same phase, examples include gas-phase decomposition of many substances, such as acetaldehyde and diethyl ether, catalyzed by iodine, and liquid-phase esterification reactions, catalyzed by mineral acids (Ronald *et al*, 1999).

2.1.4 Catalyst Supports

A catalyst support is a material, usually solid with a high surface area, to which active specie(s) of a catalyst is dispersed. For instance, the reactivity of heterogeneous catalysts occurs at the surface atoms, consequently great effort is needed to maximize the surface area of such catalyst, and also ensure high dispersion of the active ingredients. The support may be inert or participate in the catalytic reactions. Typical supports include various kinds of carbon, alumina, and silica (Zhen and Francisco, 2006). Delmon *et al* (2005) emphasized on commonly used support products, which include: alumina, zeolites, monolith cordierite, diatomaceous earth, activated carbon, silica gel, silica/alumina, activated clay, and magnesia.

Almost all major catalysts are supported, even Mo-Co-S materials, which are often regarded as the largest scale classes of catalysts are supported on alumina. They are used for hydrodesulfurization. In the area of organic synthesis, palladium (supported on charcoal) is a common hydrogenation catalyst. Also, the Ziegler-Natta olefin polymerization uses titanium chloride catalysts supported on magnesium chloride (Zhen and Francisco, 2006).

2.1.5 Explanations of some used terms

(i) Poisoning

Poisoning is the strong chemisorption of reactants, products or impurities on sites otherwise available for catalysis. A catalyst is poisoned when the chemisorped species blocked the sites for catalytic reaction.

(ii) Fouling, Coking and Carbon Deposition

Fouling is the physical (mechanical) deposition of species from the fluid phase onto the catalyst surface and in catalyst pores, which results in activity loss due to blockage of sites and/or pores. In its advanced stages it may result in disintegration of catalyst particles and plugging of the reactor voids. Important examples include mechanical deposits of carbon and coke in porous catalysts. Although carbon- and coke-forming processes also involve chemisorptions of different kinds of carbons or condensed hydrocarbons which may act as catalyst poisons. Carbon is typically a product of CO disproportionation while coke is produced by decomposition or condensation of hydrocarbons on catalyst surfaces and typically consists of polymerized heavy hydrocarbons.

(iii) Sintering

Sintering refers to the loss of catalytic surface area due to crystallite growth of the catalytic phase or due to pore collapse on crystallites of the active phase. It is also the loss of support area due to pore collapse. Sintering processes generally take place at high temperatures (e.g greater than 500^0C) and are generally accelerated by the presence of water vapour, (Bartholomew, 2001).

Catalyst Performance

Performance of a catalyst may be described in terms of activity, selectivity and stability.

(iv) Activity

Catalytic activity is the augmentation of the rate and energy of a chemical reaction by a catalyst. Activity is any change-increase or decrease in the reaction’s rate. A more active catalyst is able to achieve the same product yield or severity at a lower reaction temperature relative to a less-active catalyst.

(v) Selectivity

The selectivity of the catalyst refers to the relative yield of desired product compared to another catalyst operating with the same severity target under similar process parameters (pressure, weight hourly space velocity-WHSV, H_2/HC). As with most reaction systems, high selectivity is desired as long as the performance can be maintained.

(vi) Stability

Stability is a measure of how long a desired performance can be maintained and it usually reflects the coking tendency of the catalyst as it affects both activity and selectivity. Higher stability in a fixed-bed catalyst translates into a longer cycle length while meeting process severity targets-i.e, more profitable on-stream time. For reforming units equipped with continuous catalyst regeneration (CCR), higher stability means lower coking tendencies and slower regeneration cycles, thereby adding operational flexibility. Such operating flexibility provides opportunities to process more demanding feed, such as higher endpoint feed or an increased catalyst life resulting from a reduced regeneration frequency. Higher catalyst stability can also allow reducing the recycle gas requirement, thus lowering operating costs; (Le Goff *et al*, 2012)

(vii) Turn Over Frequency (TOF)

The number of times that the overall catalytic reaction takes place per catalytic site per unit time for a fixed set of reaction condition: temperature, pressure or concentration, reactant ratio, extent of reaction.

TOF = number of molecules of a given product/(number of active sites)/time

2.2 CHEMISTRIES OF PLATINUM, ZINC AND ALUMINA

2.2.1 Platinum

Platinum is a malleable, dense, ductile, precious, gray-white transition metal that is very resistant to corrosion. It is used to make jewelry, wire, electrical contacts and laboratory vessels. Platinum expands at nearly the same rate as soda-lime-silica glass, it is used to make sealed electrodes in glass systems. Platinum is used to coat missile nose cones, jet engine fuel nozzles and other devices that must operate reliably for long periods of time at high temperatures. Platinum resistant wires are used in high temperature electric furnaces. Platinum anodes are used in cathodic protection systems to prevent ships, pipelines and steel pipes from corroding in salt water. Of utmost important, platinum is widely used as a catalyst. It converts methyl alcohol vapors (CH_4O) into formaldehyde (CH_2O) on contact, glowing red hot in the process. This effect is used to make small hand warmers. Platinum is also used in a device called catalytic converter, a device found in the exhaust systems of most cars. Catalytic converters combine carbon monoxide (CO) and unburned fuel from a car's exhaust with oxygen from the air, forming carbon dioxide (CO_2) and water vapor (H_2O). Platinum is also used as a catalyst in the production of sulfuric acid (H_2SO_4) and in the cracking of petroleum products. Fuel cells, devices that combine hydrogen and oxygen to produce electricity and water, also use platinum as a catalyst (Craig and Anderson, 1995).

The most common oxidation states of platinum are +2 and +4. The +1 and +3 oxidation states are less common, and are often stabilized by metal bonding in bimetallic (or polymetallic) species. As expected, tetracoordinate platinum(II) compounds tend to adopt 16-electron square planar geometries. While elemental platinum is generally unreactive, it dissolves in aqua regia to give soluble hexachloroplatinic acid (H_2PtCl_6).

$$Pt + 4HNO_3 + 6HCl \rightarrow H_2PtCl_6 + 4NO_2 + 4H_2O \qquad (2.1)$$

As a soft acid, platinum has a great affinity for sulfur, such as on dimethyl sulfoxide (DMSO). Numerous DMSO complexes have been reported and care should be taken in the choice of reaction solvent, Han *et al* (2007). Table 2.1 gave a brief description of the basic characteristics of elemental platinum.

Table 2.1: Basic Characteristics of Platinum, (Craig and Anderson, 1995)

Characteristics	**Description**
Chemical Symbol	Pt
Atomic Number	78
Atomic Weight	195.084
Melting Point	1768.4^{0}C
Boiling Point	3825^{0}C
Density	21.46g/cm^{3}
Atomic Radius	138.8pm
Crystal structure	Cubic closed packed
Phase at Room Temp	Solid
Appearance	Grayish White
Element Category	Transition Metal
Position on the periodic table	Period 6, Group 10
Isotopes	^{190}Pt, ^{192}Pt, ^{194}Pt, ^{195}Pt, ^{196}Pt, & ^{198}Pt
Oxidation States	+2 & +4 (most common) +1 & +3 (less common)

2.2.2 Zinc

Zinc (Zn), a lustrous blue-white transition metal, has atomic number of 30amu and atomic weight of 65.39gmol^{-1}. It has 30 known isotopes ranging from Zn-54 to Zn-83. Five of these isotopes are regarded as suitable: Zn-64 (48.63%), Zn-66 (27.90%), Zn-67 (4.10%), Zn-68 (18.75%) and Zn-70 (0.60%). Zinc has melting point of 419.58^{o}C, boiling point of 907^{0}C, specific gravity of 7.133 (at 25^{0}C), with a valency of 2. Zinc has atomic radius of 134pm, and a hexagonal close-packed crystal structure. Zinc is brittle at low temperature, but becomes malleable at 100-150^{0}C. It is a fair electrical conductor. Zinc burns in air at red heat evolving white clouds of zinc oxide.

Zinc is a fairly active element. It dissolves in both acids and alkalis. It will react with dilute acids to release hydrogen. Zinc is used: to form alloys, to galvanize other metals to prevent corrosion, as an essential element for humans/animals nutrition. The primary ores of zinc are sphalerite or blende (zinc sulfide), smithsonite (zinc carbonate), calamine (zinc silicate), and franklinite (zinc, iron, and manganese oxides), Bentor (2014).

2.2.3 Alumina

Alumina is a common name for aluminium oxide (Al_2O_3) which is an amphoteric oxide. Al_2O_3 is found in nature in the minerals corundum (Al_2O_3), diaspore ($Al_2O_3 \cdot H_2O$), gibbsite ($Al_2O_3 \cdot 3H_2O$) and most commonly in bauxite (an impure form of gibbsite). Al_2O_3 is the only oxide formed by the metal aluminum. Largely, alumina is obtained from the mining and refining of the deposits of bauxite ore. Australia is the largest alumina refiner in the world, processing nearly one-third of the global total. Alumina, in its activated form, is used for a wide range of adsorbent and catalyst applications including the adsorption of catalysts in polyethylene production, in hydrogen peroxide production, as a selective adsorbent for many chemicals including arsenic, fluoride, in sulfur removal from gas streams. Alumina, whose basic properties are given in Table 2.2, is also used in the manufacture of abrasives, artificial rubies and sapphires, (George, 2008). Fig 2.2 shows typical alumina sample while Fig 2.3 shows its crystalline structure.

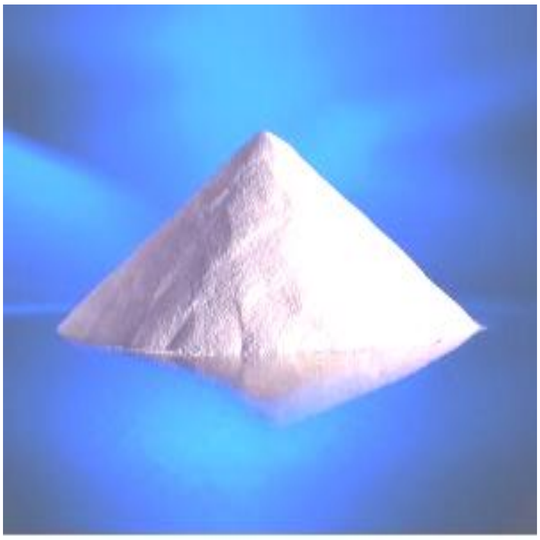


Figure 2.2: Alumina sample (www.alibaba.com)

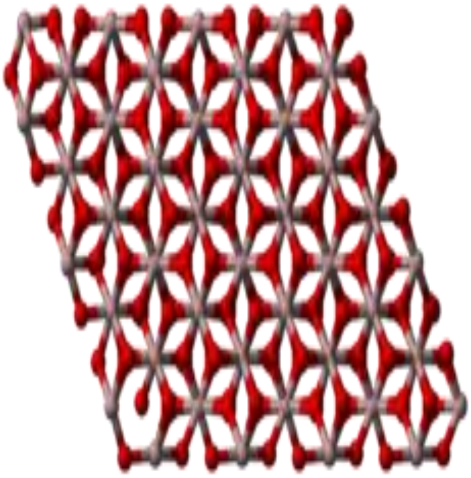


Figure 2.3: Crystal structure of aluminium oxide (Bawa, 2012)

Table 2.2: Basic properties of alumina (Bawa, 2012)

Properties	**Descriptions**
Appearance	White Solid
Molecular Formular	Al_2O_3
Molar Mass	$101.96gmol^{-1}$
Density	$3.95 - 4.1g/cm^3$
Melting Point	2072^0C
Boiling Point	2977^oC
Solubility	Insoluble

2.2.3.1 *Gamma-Alumina* 16

Nanocrystalline gamma-phase alumina (γ-Al_2O_3) is among many polytypes of alumina that find extensive application as a catalyst and catalysts support. The most useful properties of these aluminas that enhanced it as a catalyst support are high specific surface area (15-300m^2/g), high thermal stability, outstanding mechanical properties and well defined porosity. The crystal has a porous texture and is a widely used industrial product as catalyst and adsorbent and it can be produced from different precursors with different crystal shapes (Bawa, 2012).

2.3 ESSENTIALS OF PLATINUM-ON-ALUMINA CATALYST

Most catalysts are definite and/or specific in action, so it is with platinum-alumina catalyst. Many reactions (such as naphtha reforming processes) will proceed much faster in the presence of the catalyst. Conversely, such processes or reactions would not practically be possible without it.

The catalyst has been widely used in chemical industry. Common applications are found in:

1. Catalytic naphtha reforming
2. Reductive alkylation of haloanilines, and halonitroaromatics,
3. Hydrogenation of aromatic nitriles, oximes,and pyridlines,
4. Catalytic oxidation of exhaust gases.

Table 2.2.1 listed the companies that are globally recognized as manufacturers of Pt/Al_2O_3 catalyst (Acres *et al*, 1999). The peculiar properties of this catalyst (see Table 2.3) also contributed largely to its vast industrial usages.

Table 2.2.1: Global manufacturers of Pt/Al_2O_3 catalyst

S/N	Company's Name	Location
1.	Zibo Wufeng Aluminum Magnesium Technology Co., Ltd	China (Mainland)
2.	Oceanus Industrial International Limited	Hong Kong
3.	RAJEXIM	United King
4.	Catalysts and Technologies	India

Table 2.3: Physical properties of a typical platinum-alumina catalyst (Roberts, 2000)

Properties	Description
Appearance	Grey/white powder, spheres or pellets
Odour	No colour
Density	Variable; about 4gm/cc, depending on the form and metal loading
Flammability	Not flammable
Explosive Properties	Not explosive
Melting Point	2020^0C for alumina
Boiling Range/Point	2980^0C for alumina
Solubility in water	Insolube
Oxidising properties	Not oxidizing

2.3.1 Dispersion of Platinum

Pt/Al_2O_3 catalyst often has lesser degree of dispersion compared to those with an addition of zinc prior to the incorporation of platinum on the alumina. George *et al* (1996) averred that the latter shows an obvious increase of dispersion of the noble metal (platinum) relative to the former. To achieve best dispersion, the impregnation of the metals (Zn and Pt) should be done sequentially, whereby Zn is impregnated prior to Pt. Impregnation of the γ-alumina with the zinc component (using a soluble zinc salts) will cause the formation of $ZnAl_2O_4$ surface-like spinels, thus, preventing the reduction of the zinc to zinc metal. The $ZnAl_2O_4$ spinels will prevent the formation of undesirable noble metal-zinc alloy. The noble metal (Pt) will be attached to the Zn^{2+} of the spinel aiding in the dispersion of the noble metal, (George *et al*, 1996).

Hydrogen and oxygen chemisorptions may be used to determine the fraction of surface occupied by platinum; and the uniformity of its distribution (dispersion) on the support matrix. Dispersion needs to be maximized and maintained for efficient use of the active metal and for best catalyst performance.

2.4. NAPHTHA

Naphtha normally refers to a number of different flammable liquid mixtures of hydrocarbons, i.e. a component of natural gas condensate or a distillation product from petroleum or coal tar boiling in certain temperature range and containing certain hydrocarbons. It is a broad term covering the lightest to the majority of the volatile fractions of the liquid hydrocarbons in petroleum. Naphtha is a colorless to reddish-brown volatile aromatic liquid, very similar to gasoline.

Full range naphtha is defined as the fraction of hydrocarbons in petroleum boiling between 30 and 200°C (Kjell *et al*, 2004). It consists of a complex mixture of hydrocarbon molecules generally having between 5 and 12 carbon atoms. It typically constitutes 15–30% of crude oil, by weight. Light naphtha is the fraction boiling between 30 and 90°C and consists of molecules with 5–6 carbon atoms. Heavy naphtha boils between 90 and 200°C and consists of molecules with 6–12 carbons, and n-octane (C_8H_{18}) is a peculiar example in this category.

Naphtha is used primarily as feedstock for producing high octane gasoline (via the catalytic reforming process). It is also used in the bitumen mining industry as a diluent, while in the petrochemical industry for producing olefins in steam crackers, and in the chemical industry for solvent (cleaning) applications. Common products made with it include lighter fluid, fuel for camp stoves, and some cleaning solvents.

2.4.1 Naphtha Production in the Refineries

Naphtha is obtained in petroleum refineries as one of the intermediate products from the distillation of crude oil. It is a liquid intermediate between the light gases in the distilled crude oil and the heavier liquid kerosene (Carl, 2013). Naphthas are volatile, flammable and have a specific gravity of about 0.8, and boiling temperature range of 30 to 200^0C. The generic name 'naphtha' describes a range of different refinery intermediate products.

2.4.2 Properties of Naphtha

Table 2.4 shows the properties of typical naphtha while Table 2.5 shows its composition.

Table 2.4: Properties of a typical naphtha, (API, 1994)

S/No	Properties	Descriptions
1	From	Liquid
2	Appearance	Colourless to light yellow
3	Odour	Characteristic hydrocarbon-like
4	Molecular Weight	100-215g/mol
5	Specific Gravity	0.77, (for H_2O)
6	Boiling Point	30-200^{0}C
7	Vapour Pressure	Less than 5 torr (5mmHg)
8	Water Solubility	Negligible
9	Percent volatiles	100%

Table 2.5: Composition of typical naphtha, (API, 1994)

Composition	Concentration (wt%)
Aromatics	13.88
Olefins	0.11
Paraffins	55.35
Naphthenes	30.70

2.4.3 Uses of Naphtha

An exhaustive account of naphtha usages may be too enormous due to its versatility. Naphtha is used for the production of numerous viable products. Although, Huebner, 1999 gave account of the most common usage as follows:

(i) Gasoline

Olefinic hydrocarbons that result from processes in some refineries result in olefin-containing naphtha, or cracked naphtha, which is used to produce high-octane elements of gasoline.

(ii) Solvents

Specialty naphthas give rise to a number of products used as solvents, like cleaning fluids, dilution agents for asphalt, paints and varnish. They are also used within the rubber industry and in dry cleaning operations. Alternative names for some of these chemicals are petroleum spirits, mineral spirits, petroleum ether, varnish makers' and painters' naphtha, white gas or white oil, paraffin, hexanes and ligroin.

(iii) Fuels

Specialty naphthas are also used in portable camping stoves, lanterns, blowtorches and cigarette lighters as fuel. Because of the bright, clean burn, naphtha is used in performance equipment for fire juggling or fire spinning.

(iv) Other Products

Paraffinic light naphthas are cracked until the molecules break apart. The resulting hydrocarbons are used to produce plastics like polypropylene and polyethylene, synthetic fibers like acrylonitrile, and industrial chemicals like glycols. Different kinds of naphthas are also used in shoe polishes and to remove oil from camera aperture blades. (Gary and Handwerk, 1984). Naphtha also finds vital application as Feedstock for Petrochemical Processes.

2.4.4 Reforming and Reformate

Reforming is an oil refining operation that produces reformate, a high-octane gasoline blending component. Reformate is one of the several blending components in finished gasoline.

The reforming process uses heavy naphtha, which is the second lightest liquid stream from an atmospheric distillation column, to produce reformate. Reformate is a component of finished gasoline. Other components of gasoline include alkylate from the alkylation unit, naphtha and straight run gasoline from the atmospheric distillation unit, cracked gasoline from the fluid catalytic cracker and coker, and hydrocrackate, which is gasoline from the hydrocracker. The amount of each component in finished gasoline depends on the particular specifications of the gasoline blend.

In the reforming complex, a feed pre-treater removes sulfur from the reformer feed using hydrogen and a desulfurization catalyst. The pre-treated feed then is sent to the reformer reactors where catalyst and heat are used to restructure or reform low octane naphtha into higher octane hydrocarbon molecules that are valuable gasoline blending components. The process turns straight-chain hydrocarbons into cyclic compounds. The cyclic compounds have a much higher octane rating than the straight-chain feedstock and enable economic production of high-octane lead-free gasoline. The process also re-shapes normal butane into a mixture of isobutane and normal butane. Isobutane has a higher octane and higher vapor pressure than normal butane. Isobutane is a gasoline blending component or a feedstock to the alkylation unit used to produce alkylate, another gasoline blending component.

Because reformate contains significant amounts of benzene, toluene, and xylene, it is also an important source of feedstock for the petrochemical industry. One of the byproducts of reforming is hydrogen, which can itself be used in other refining processes or sold for other industrial use.

Clear disparities in composition exist between naphtha and reformate, (refer to Table 2.5, and Table 2.6). Naphtha comprises of very small portion of aromatics and olefins, and large proportion of paraffins and naphthenes. Conversely, reformate consist largely of aromatics with smaller proportion of paraffins and naphthenes. The composition of a typical reformate as given by API, 1994 is shown in Table 2.6.

Table 2.6: Reformate Composition (API, 1994)

Composition	**Mass %**
Aromatics	72.56
Paraffins	25.56
Naphthenes	1.06
Olefins	0.82

2.4.4.1 *Uses of Reformate*

In addition to the use of reformate as a blending component of motor fuels, it is also a primary source of aromatics used in the petrochemical industry (Huebner, 1999). The reformate stream from a catalytic reforming unit is invariably used either as a high octane gasoline blending component or as a source of aromatics- benzene, toluene, and xylenes, (BTX) and C_{9+} aromatics. Reforming for motor fuel applications still represents the majority of existing reforming capacity.

Reformate specifications (octane, vapor pressure, end point, etc.) are set to provide an optimum blending product. The octane requirement is met through the production of high-octane aromatics, the isomerization of paraffins, and the removal of low octane components by cracking them to gaseous products. Feedstocks to these units are typically “full range” naphthas, consisting of hydrocarbons with 6–12 carbon atoms; however, the initial boiling point may be varied to limit the presence of benzene precursors. Reforming units for the production of aromatics are often called BTX reformers.

Naphthas for these units are specified to contain mostly naphthenes and paraffins of 6–8 carbons. The desired reaction is aromatization through dehydrogenation of the naphthenes, and cyclization and dehydrogenation of the paraffins to the analogous aromatic (API, 1994).

2.5 NAPHTHA REFORMING PROCESSES

Catalytic reforming is a major petroleum refining process used to raise the octane rating of heavy naphthas (C_6 to C_{12} hydrocarbons) for gasoline blending. Catalytic reforming is also a principal source of aromatic compounds, i.e., benzene, toluene and xylenes, via conversion of paraffins and naphthenes to aromatics.

Upgrading by reforming may be accomplished, in part, by an increase in volatility (reduction of molecular size) or by the conversion of n-paraffins to isoparaffins, olefins, and aromatics, and of naphthenes (cycloalkanes) to aromatics. The nature of the final product is influenced by the structure and composition of the straight-run (virgin) naphtha, (James 2010).

The principal reforming chemical reactions are dehydrogenation of cyclohexane to aromatics, dehydro-cyclization of paraffins to aromatics, dehydroisomerization of alkylcyclopentanes to aromatics, isomerization of normal paraffins to branched paraffins, dealkylation of alkylbenzenes, and hydrocracking of paraffins to light hydrocarbons. The hydrocracking of paraffins to light hydrocarbons is undesirable and should be minimized because light hydrocarbons have low octane value (Kao and Ramsey, 2011).

2.5.1 Feedstocks

Naphtha feedstocks to reformers typically contain paraffins, naphthenes, and aromatics with 6–12 carbon atoms. Most feed have to be hydrotreated to remove metals, olefins, sulfur, and nitrogen, prior to being fed to a reforming unit. A typical straight run naphtha from crude distillation may have a boiling range of 150–400^{0}F (65–200^{0}C), Carl (2013).

In addition to naphthas from crude distillation, naphthas can be derived from a variety of other processes that crack heavier hydrocarbons to hydrocarbons in the naphtha range. Cracked feedstocks may be derived from catalytic cracking, hydrocracking, cokers, thermal cracking, as well as visbreaking, fluid catalytic cracking, and synthetic naphthas obtained, for example, from a Fischer–Tropsch process.

In the work of George *et al* (2005) it was confirmed that light paraffinic naphthas are more difficult to reform than heavier naphthenic hydrocarbons. Furthermore, the distillation values for the initial boiling point, the mid-point at which 50% of the naphtha is distilled over, and the end point are often used to characterize a naphtha. Feed hydrotreating is used to reduce feedstock contaminants to acceptable levels. Common poisons for reforming catalysts that are found in naphtha are sulfur, nitrogen, and oxygen compounds. Removing these requires breaking of a carbon-sulfur, -nitrogen or -oxygen bond and formation of hydrogen sulfide, ammonia, or water, respectively. Hydrotreaters will also remove olefins and metal contaminants.

2.5.2 Typical Catalysts

Catalysts commonly used in commercial reformers include a Group 10 metals, such as platinum, or platinum plus a second catalytic metal, such as rhenium or iridium, dispersed on an alumina substrate. The suitability of using zinc as the second metal is to be verified herein. Typically, chlorine is incorporated on the alumina to add acid functionality. Alumina-based reforming catalysts are suitable for aromatizing C_8+ paraffins, but are less effective for aromatizing C_6 to C_8 paraffins because these catalysts hydrocrack more of the lighter paraffins to low value fuel gas than converting them to aromatics (API, 1994).

2.5.3 The Process Chemistry

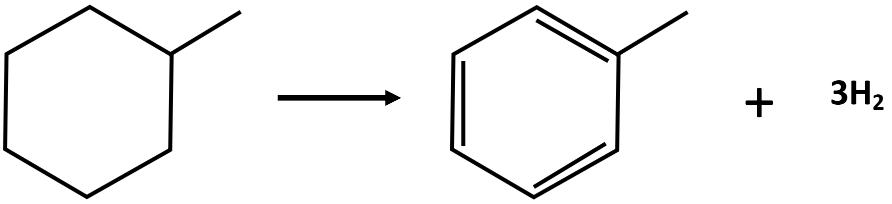
There are many chemical reactions that occur in the catalytic reforming process, all of which occur in the presence of a catalyst and a high partial pressure of hydrogen. Depending upon the type or version of catalytic reforming used as well as the desired reaction severity, the reaction conditions range from temperatures of about 495 to 525°C at pressures of about 5 to 45 atm. (OSHA, 2005).

The commonly used catalytic reforming catalysts contain noble metals such as platinum and/or rhenium, which are very susceptible to poisoning by sulfur and nitrogen compounds. Therefore, the naphtha feedstock to a catalytic reformer is always pre-processed in a hydrodesulfurization unit which removes both the sulfur and the nitrogen compounds.

According to Gary and Handwerk (1984), the major catalytic reforming reactions are:

(1). The dehydrogenation of naphthenes to convert them into aromatics. The dehydrogenation of naphthenes, or aromatization, occurs when a cyclohexane ring within the compound stabilizes itself by forming a benzene ring, releasing three hydrogen molecules in the process. This process is both endothermic and extremely fast (by over four orders of magnitude faster than the next preceding reaction rate). A typical example is the conversion of methylcyclohexane (a naphthene) to toluene (an aromatic), as shown in equation 2.2.

$$C_7H_{14} \longrightarrow C_7H_8 + 3H_2 \tag{2.2}$$

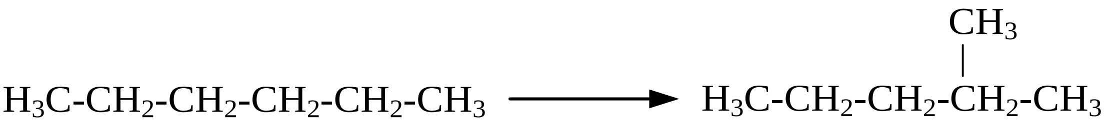


(2.3)

(2). The isomerization reaction is one in which a section of non-branched or partly-branched hydrocarbon chain is shifted to another location on the base carbon chain, creating an isoparaffin or an isomer of the base ring compound. This reaction is split into four different reaction families based on the method by which the isomerizing chain is initially removed, then reattached to the base hydrocarbon chain (either from alpha, beta 1, beta 2, or gamma scission). This reaction, while not nearly as fast as the aromatization reaction, is still fairly fast compared to rate limiting reactions such as cracking. Furthermore, isomers are far more desirable than aromatics from an ecological standpoint, as isomers still produce high octane ratings while being better for biodegrading than highly stable aromatics (Carl, 2013).

The isomerization of normal paraffins to isoparaffins is exemplified in the conversion of:

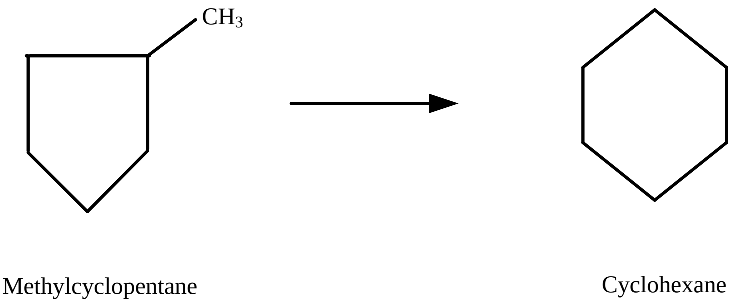
(a) normal hexane to isohexane, and (b) methylcyclopentane to cyclohexane, as shown in the following reaction schemes:



$$H_3C-CH_2-CH_2-CH_2-CH_2-CH_3 \longrightarrow H_3C-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}H_2-CH_3$$

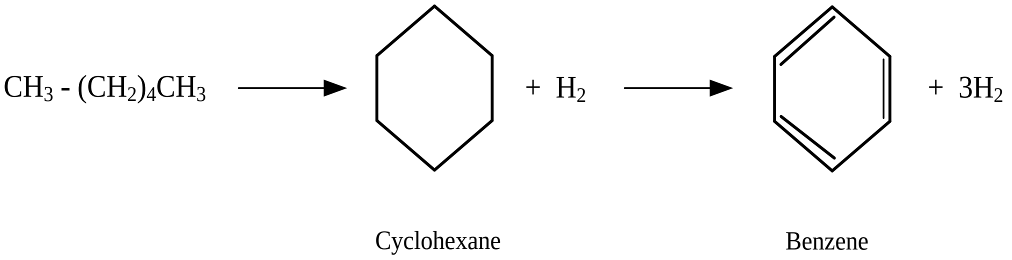
Hexane Isohexane

(2.4)



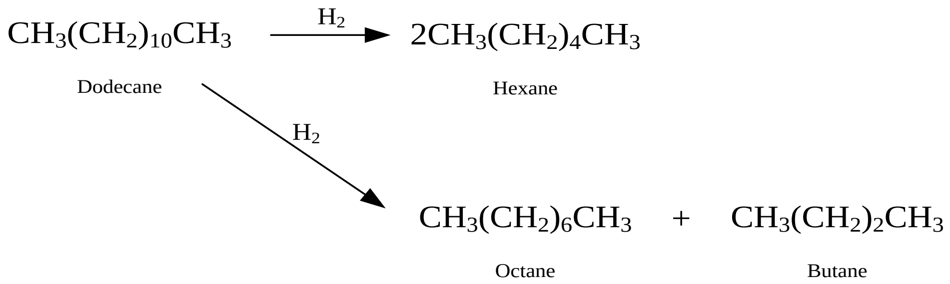
(2.5)

(3). The dehydrogenation and aromatization of paraffin compounds to aromatic compounds is commonly called dehydrocyclization. This is a ring formation reaction in which a paraffin or isoparaffin is brought into a five or six member ring, releasing one hydrogen molecule in the process. Paraffin dehydrogenation reaction, which is a necessary precursor to the formation of aromatics, is quite a few orders of magnitude slower than dehydrogenation of naphthenes-aromatization, and therefore is the limiting reaction in aromatic formation.



(2.6)

(4). Hydrocracking: Paraffin cracking is the process by which larger paraffins and i-paraffins are broken down into smaller fragments. Hydrocracking is an hydrogen consuming reaction, and it often leads to yield loss in the form of C_1-C_4 compounds, which do not stay in liquid form. These reactions occur at a far slower pace than isomerization or ring formation, (Carl, 2013).



(2.7)

The conversion of cyclic paraffins and n-paraffins to aromatics is most important because of the high octane of the resulting aromatic product compared to the low octane of the n-paraffin feedstock. The octane number is increased by aromatization of paraffin components and dehydrogenation of naphthenes to aromatics.

Note that: the hydrocracking of paraffins is the only one of the above four major reforming reactions that consumes hydrogen. The isomerization of normal paraffins does not consume or produce hydrogen. However, both the dehydrogenation of naphthenes and the dehydrocyclization of paraffins produce hydrogen. Other reforming reactions include:

(5). Ring Isomerization

This is the isomerization of a five-membered ring into a six-membered ring. The transformation of a cyclopentane to a cyclohexane is the necessary pathway for a five-membered ring to be transformed into an aromatic. This isomerization reaction is far slower than all other isomerization reactions, given that the system is already stable in a five-membered ring formation. This slows the formation of aromatics slightly, allowing for mid-sided paraffins and isoparaffins to still exist without being consumed completely into aromatics, (Carl, 2013).

(6). Dehydroisomerization of alkylcyclopentanes to aromatics

During reforming, aromatic hydrocarbon compounds can be produced by dehydroisomerization of five membered naphthene ring hydrocarbons. The alkylcyclopentanes is first isomerizes to cyclohexane and its homologues; followed by dehydrogenation of cyclohexane rings. During the reaction, the feed is contacted with a reforming catalyst at a temperature between 454.4^0C-537^0C, in the presence of added or recycled hydrogen and under a pressure of about $7.0kg/cm^2$. As a result of such operation, alkylated five membered naphthene ring compounds are converted to aromatic hydrocarbons, (Carl, 2013).

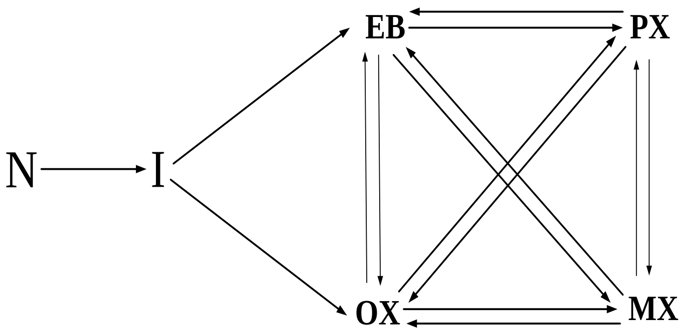
(7). Dealkylation of alkylbenzene

This is a form of side chain cracking reaction in which an alkylbenzene is defragmented into a ring species and a paraffin or isoparaffin, thus producing far smaller aromatic products. The reaction rate of dealkylation is very low, with fairly large activation energy.

The overall net production of hydrogen in the catalytic reforming of petroleum naphthas ranges from about 50 to 200 cubic meters of hydrogen gas (at 0°C and 1 atm) per cubic meter of liquid naphtha feedstock (Kjell *et al*, 2004). In many petroleum refineries, the net hydrogen produced in catalytic reforming supplies a significant part of the hydrogen used elsewhere in the refinery (for example, in hydrodesulfurization processes). The hydrogen is also necessary in order to hydrogenolyze any polymers that form on the catalyst.

2.5.3.1 *n-octane reforming reaction*

The reforming of n-octane can be considered a peculiar form of naphtha reforming, as n-octane is a member of the heavy naphtha fraction. Susu *et al* (2005) gave the reaction scheme for the catalytic reforming of n-octane (N) on Pt/Al_2O_3 catalyst to form ethylbenzene (EB), ortho- xylene (OX), para-xylene (PX), and meta-xylene (MX) as follows:



(2.8)

(where I represents iso-octane)

2.6 THE CATALYTIC REFORMING UNIT (CRU) IN THE REFINERIES

The most commonly used type of catalytic reforming unit has three reactors, each with a fixed bed of catalyst, and all of the catalyst is regenerated in-situ during routine catalyst regeneration shutdowns which occur biennially in most refineries. Such a unit is referred to as a semi-regenerative catalytic reformer (SRR).

Some catalytic reforming units have an extra spare or swing reactor and each reactor can be individually isolated so that any one reactor can be undergoing in situ regeneration while the other reactors are in operation. When that reactor is regenerated, it replaces another reactor which, in turn, is isolated so that it can then be regenerated. Such units, referred to as cyclic catalytic reformers, are not very common. Cyclic catalytic reformers serve to extend the period between required shutdowns.

The latest and most modern type of catalytic reformers are called continuous catalyst regeneration reformers (CCR). Such units are characterized by continuous in-situ regeneration of part of the catalyst in a special regenerator, and by continuous addition of the regenerated catalyst to the operating reactors. As of 2005, the two CCR versions available are: UOP's CCR Platformer process and Axen's Octanizing process. The installation and use of CCR units is rapidly increasing (OSHA, 2005).

The process flow diagram shown in Figure 2.4 depicts a typical semi-regenerative catalytic reforming unit.

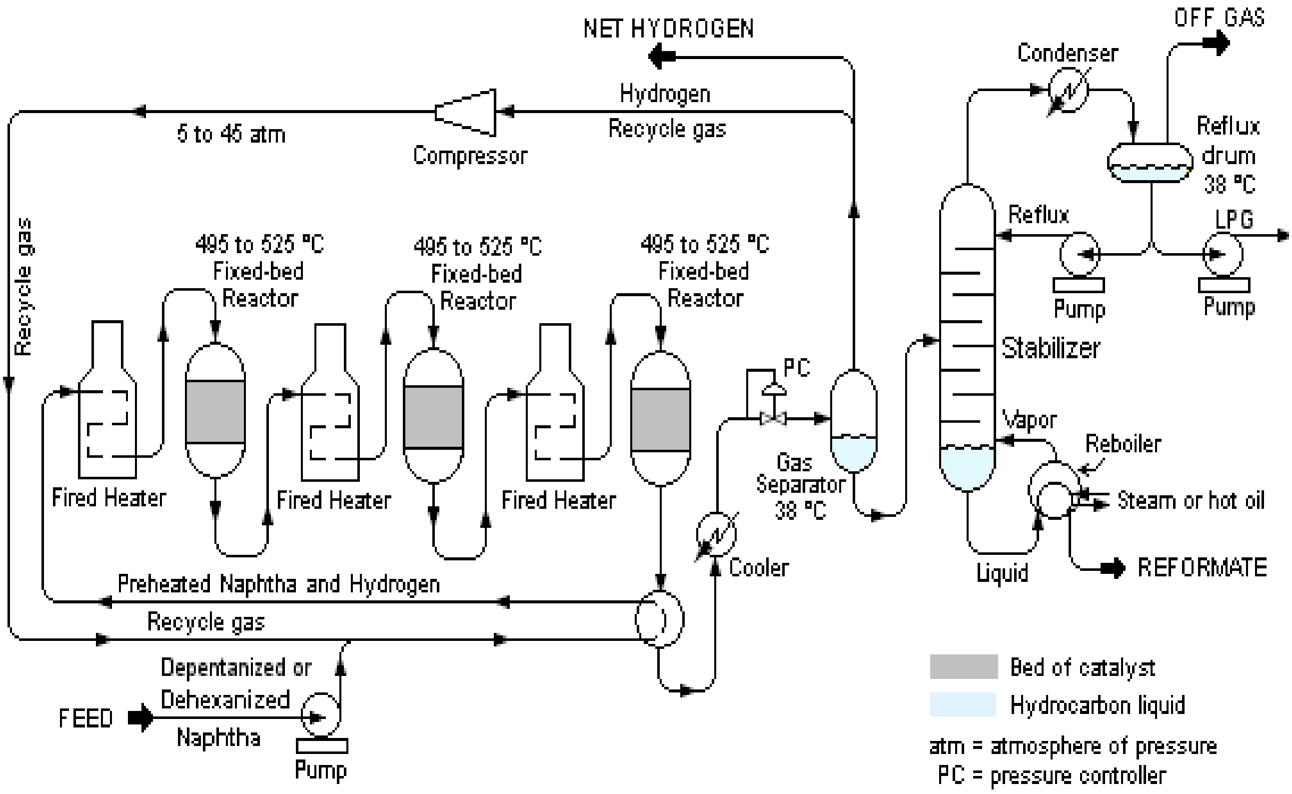


Figure 2.4: Schematic diagram of a typical semi-regenerative catalytic reformer unit in a petroleum refinery (Gary and Handwerk, 1984).

The liquid feed (at the bottom left in the diagram) is pumped up to the reaction pressure (5 to 45 atm) and is joined by a stream of hydrogen-rich recycle gas. The resulting liquid-gas mixture is preheated by flowing through a heat exchanger. The preheated feed mixture is then totally vaporized and heated to the reaction temperature (495 to 520 °C) before the vaporized reactants enter the first reactor. As the vaporized reactants flow through the fixed bed of catalyst in the reactor, the major reaction is the dehydrogenation of naphthenes to aromatics which is highly endothermic and results in a large temperature decrease between the inlet and outlet of the reactor. To maintain the required reaction temperature and the rate of reaction, the vaporized stream is reheated in the second fired heater before it flows through the second reactor. The temperature again decreases across the second reactor and the vaporized stream must again be reheated in the third fired heater before it flows through the third reactor.

As the vaporized stream proceeds through the three reactors, the reaction rates decrease and the reactors therefore become larger. At the same time, the amount of reheat required between the reactors becomes smaller. Usually, three reactors are all that is required to provide the desired performance of the catalytic reforming unit. Some installations use three separate fired heaters as shown in the schematic diagram and some installations use a single fired heater with three separate heating coils.

The hot reaction products from the third reactor are partially cooled by flowing through the heat exchanger where the feed to the first reactor is preheated and then flow through a water-cooled heat exchanger before flowing through the pressure controller (PC) into the gas separator. Most of the hydrogen-rich gas from the gas separator vessel returns to the suction of the recycle hydrogen gas compressor and the net production of hydrogen-rich gas from the reforming reactions is exported for use in the other refinery processes that consume hydrogen (such as hydrodesulfurization units and/or a hydrocracker unit).

The liquid from the gas separator vessel is routed into a fractionating column commonly called a stabilizer. The overhead offgas product from the stabilizer contains the byproducts methane, ethane, propane and butane gases produced by the hydrocracking reactions, and it may also contain some small amount of hydrogen. The off-gas is routed to the refinery's central gas processing plant for removal and recovery of propane and butane. The residual gas after such processing becomes part of the refinery's fuel gas system. The bottoms product from the stabilizer is the high-octane liquid reformate that will become a component of the refinery's product gasoline (OSHA, 2005).

2.7 PREPARATION OF Pt-Zn/Al_2O_3 CATALYST

Dispersion and Calcination Method

Dispersion entails the incorporation of a catalytically active species onto a support material. It involves rendering a metal-salt component into a finely-divided-form on a support. A wide range of techniques has been employed for this purpose. They include: impregnation, adsorption from solution, co-precipitation, or deposition.

Impregnation (which was used herein) entails use of solution to dope the support. Such solution can be a neutral salt or acid solution having the respective component(s) dissolved therein. If for instance, $ZnCl_2$ is used, the solution should be acidic to facilitate dissolution of the salt. Suitable zinc and noble metal salts are: all soluble zinc salts such as zinc acetate, zinc chloride, zinc bromide, zinc fluoride, zinc carbonate, zinc nitrate or any other soluble zincate salt and any of the soluble noble metal salts or complexes such as ammonium chloroplatinate, dinitrodiamino platinum, chloroplatinic acid, bromoplatinic acid or any of the other soluble noble metal salts or complexes. It is preferred to use the halide salts of zinc and noble metal to incorporate the necessary halide of the composition in a single step. Preferably the chloride salts will be used.

Calcination or Reduction is brought about by a thermal treatment in either an inert atmosphere or an active atmosphere of either oxygen or hydrogen. When the active atmosphere is hydrogen the process is known as reduction (Yusof *et al*, 1996).

The reactions taking place during the calcination and reduction processes for Pt-Zn/Al_2O_3 catalyst preparation are:

$ZnCl_2$ and gamma-alumina mixture:

Calcination:

$$ZnCl_2 \xrightarrow{500^0C} ZnCl_2 + Volatile\ \ components \uparrow \tag{2.9}$$

Reduction:

$$ZnCl_2 \xrightarrow[Under\,H_2\ Flow]{500^0C} 2HCl + Zn \tag{2.10}$$

Dried Zn/Al_2O_3 matrix and H_2PtCl_6 mixture:

Calcination:

$$H_2PtCl_6 \xrightarrow{500^0C} PtCl_4 + 2HCl \uparrow \tag{2.11}$$

Reduction

$$PtCl_4 \xrightarrow[Under\ H_2\ Flow]{500^0C} 4HCl + Pt \tag{2.12}$$

2.7.1 Description of the Catalyst

Pt-Zn/Al_2O_3 catalyst is a bimetallic catalyst having both metals platinum and zinc supported on a porous, large surface area alumina as a carrier. The catalyst is bifunctional; acid-catalyzed, and metal catalyzed. Platinum supplied the metal function by providing the essential sites for hydrogenation and dehydrogenation.

The acid function is provided by the acidified gamma-alumina, which basically catalyze isomerization and cyclization reactions. Gamma-alumina is amphoteric, thus the need for the addition of chlorine to promote its acidity.

The inclusion of zinc in appropriate amount is mainly to improve the platinum dispersion and as well enhanced better performances in terms of catalyst selectivity and resistance against deactivation. Luciene *et al* (2012) and Yiwei *et al* (2012) concluded in their works that bimetallic catalysts of this nature show better performances than monometallic catalysts.

2.8 CATALYST CHARACTERIZATION

Theory of Analyses

The fundamental basic principles underlining each of the analytical method used are enumerated hereunder:

2.8.1 Basic principles of BET analysis

Brunauer-Emmett-Teller (BET) theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. The first article on BET theory was published by Stephen Brunauer, Paul Huge Emmett, and Edward Teller in 1938, (Brunauer *et al*, 1938).

The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypothesis: (a) gas molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer. The resulting equation is.

$$\frac{1}{v\left[\left(P/P_0\right)-1\right]}=\frac{1}{v_m c}+\frac{c-1}{v_m c}\left(\frac{P}{P_0}\right) \qquad \textbf{(2.13)}$$

Where *P* and *P*$_0$ are the equilibrium and the saturation pressures of the absorbates at the temperature of adsorption.

v **is the adsorbed gas quantity (for example, in volume units).**

v_m **is the monolayer adsorbed gas quantity.**

c **is the BET constant.**

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right) \tag{2.14}$$

E_1 is the heat of adsorption for the first layer, and *E_L* is the second and higher layers and is equal for the heat of liquefaction.

Equation (2.13) is an adsorption isotherm and can be plotted as a straight line with $1/v\left[(P_0/P)-1\right]$ on the *y*-axis and P/P_0 **on *x*-axis according to experimental results. This plot is called the BET Plot. The linear relation of this equation is maintained only in the range of** $0.05 < P/P_0 < 0.35$**.**

Consequently, the slope *S*, and the *y*-intercept *I* can be used to calculate the monolayer adsorbed gas quantity v_m **and the BET constant** c**.**

i.e $A = \frac{c-1}{v_m c}$**, and** $I = \frac{1}{v_m c}$ **(2.15)**

From equation (2.15), $c = \frac{1}{I v_m}$ **and** $v_m = \frac{c-1}{cA}$ **(2.16)**

By appropriate substitutions in (2.16),

$$v_m = \frac{1}{A + I} \tag{2.17}$$

The BET method is widely used in surface science for the calculation of surface areas of solids by physical adsorption of gas molecules. The total surface area *S_{total}* and the specific surface area *S_{BET}* are given by

$$S_{total} = \frac{(v_m N_s)}{V} \tag{2.18}$$

$$S_{BET} = \frac{S_{total}}{m} \qquad \textbf{(2.19)}$$

Where v_m is the units of volume which are also the units of the molar volume of the adsorbate gas, N is Avogadro's number, s the adsorption cross section of the adsorbing species, V the molar volume of the adsorbate gas, and m the mass of the adsorbent.

BET Surface Area Analyses provide precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser. The technique encompasses external area and pore area evaluations to determine the total specific surface area in m^2/g yielding important information in studying the effects of surface porosity and particle size in many applications.

2.8.2 Basic Principles of XRD Analysis

Most solid materials are crystalline in nature. When X-ray interact with a crystalline substance (phase), one get a diffraction pattern. Every crystalline substance gives a pattern; the same substance always gives the same pattern; and in a mixture of substances each produces its pattern independently of the others. The X-ray diffraction pattern of a pure substance is like a fingerprint of the substance. The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phase. The main use of powder diffraction is to identify components in a sample by a search/march procedure. Furthermore, the areas under the peak are related to the amount of each phase present in the sample. For match-making purposes, there are about 50,000 inorganic and 25,000 organic single components, crystalline phases, diffraction patterns which have been collected and stored on magnetic or optical media as standards.

Crystalline solid matters are those whose atoms are arranged in a regular pattern, and there is a smallest volume element that by repetition in three dimensions describes the crystal. Amorphous solid matters are those whose atoms are arranged in a random way similar to the disorder we find in a liquid. Glasses are amorphous material.

The Bragg Equation:

Reflection of x-rays from two planes of atoms in a solid. $X = d\sin\theta$

The path difference between two waves: 2*wavelength = $2d\sin\theta$

$$n\lambda = 2d\sin\theta \qquad (2.20)$$

Information obtainable from Powder X-ray Diffraction:

Lattice parameter

Phase identity

Phase purity

Crystallinity

Crystal structure

Percentage phase composition.

2.8.3 Basic Principles of SEM Analysis

The extent of dispersion of an active ingredient (platinum metal) on a support (γ-alumina) can be determined by Scanning electron microscopy (SEM) technique. SEM analyzes the surface of materials. It also measures and evaluates surface pitting, failure analysis, characterization of dust, deposits, contaminants, particles, filter residues, and other applications.

SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of the solid specimens. The signals derived from such electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm); Goldstein (2003).

Although, in recent time, the use of electron probe microanalysis (EPMA) is rapidly becoming standard practice for measure of metal dispersion. This gives us a relatively rapid and unambiguous method for investigating the location, not only of active materials but also potential catalyst poisons. Other known techniques for measuring metal dispersion are electron microscopy, and gas adsorption (Cody, 1994).

2.8.4 Basic Principles of GC-MS Analysis

The Gas Chromatograph/Mass Spectrometry (GC/MS) instrument separates chemical mixtures (the GC component) and identifies the components at a molecular level (the MS component). It is one of the most accurate tools for analyzing environmental samples. It is considered a powerful and widely used technique for analysis of hydrocarbons in naphthas. **GC works on the principle that a mixture will separate into individual substances when heated. The heated gases are carried through a capillary column with an inert gas (such as helium). The flow of the gases through the** dedicated column allows transport of the different molecules at different rates thus leading to separation. **As the separated substances emerge from the column opening, they flow into the MS. Mass spectrometry identifies compounds by the mass of the analyte molecule.** A flame ionization detector creates and detects a signal proportional to the concentration of each hydrocarbon as the components exit the column. It operates by collecting (by an electrode) the ions of the flame produced during combustion of the hydrocarbon. The detector response is approximately proportional to the weight of carbon present which greatly simplifies quantitative analysis.

The rate of hydrocarbon transport through the column is dependent on the carrier gas velocity, which may be adjusted based on the injector pressure and the oven temperature. The lightest hydrocarbons (methane and ethane) are transported very quickly through the column and separation requires low/ambient temperature (George *et al*, 2005).

Mass spectrometry is considered the only definitive analytical detector. It has a library of known mass spectra, covering several thousand compounds, which are stored on a computer.
It is important to note that a limitation of GC-MS could be time consumption, but with the newly developed portable GC-MS model, this challenge may be offset.

CHAPTER THREE

MATERIALS, EQUIPMENT AND METHODS

3.1 MATERIALS

Table 3.1 shows the major materials used.

Table 3.1: Materials used for the experiments

Material	**Source**	**Grade**	**Remark**
Alumina	PTDF LAB, Chem Eng Dept, ABU Zaria	-	-
Distilled water	Chemical Eng Dept, ABU.	-	-
The catalysts	Developed	-	-
n-octane	Sigma-Aldrich Co, USA	≥ 99%	Imported
Hexachloroplatinic acid	Sigma-Aldrich Co, USA	Analar	”
Zinc chloride	Sigma-Aldrich Co, USA	0.1M	”

3.2 APPARATUS

The apparatuses used in the course of the work are:

1. Beakers (Pyrex)
2. Conical flasks (500ml), Pyrex
3. Measuring cylinders (1000ml, 500ml, 10ml), Pyrex
4. Crucibles
5. Laboratory mortar and pestle
6. Spatula
7. Plastic spoons

8. Buchnel flask (1 litre)
9. Sinta glass filter
10. Glass rod stirrer
11. Thermometer (-10^{o}C to 360^{o}C)
12. Desiccators
13. Sample bottles (glass and plastic)
14. Petri dishes
15. Stainless steel thongs
16. **Tubular muffle furnace**
17. Heating mantle

3.3 EQUIPMENT

The list of equipment used for the work are detailed in Table 3.2

Table 3.2: List of other equipment used in this work and their specifications

S/N	Name	Model	Manufacturer
1	GC-MS Machine	QP2010 PLUS	Shimadzu, Japan
3	X-ray Diffractometer Machine	Empyreal	PANalytical
4	Analytical Balance, (0-180g)	AB 204	Mettler Toledo, Switzerland
5	Oven, (0-260^{0}C)	TM OV-420	Gallenkamp England
6	Tube Furnace	-	Naberthem, Germany
7	Exposed Element Furnace	TIKIR 11/12	Heraeus, Holland
8	Distilled Water Machine	A4000	Aquatron

9	Scanning Electron Microscope	Pro-X	Phenom-World Co., Holland

3.4 EXPERIMENTAL PROCEDURES

The details of the experimental procedures followed in the course of this work are given as follows:

3.4.1 Catalysts Preparation

Development of Monometallic Catalyst:

0.2161g of $ZnCl_2$ salt was dissolved in 100ml of distilled water and the mixture was well stirred to give an aqueous solution of $ZnCl_2$. In a separate beaker, 10g of gamma-alumina was immersed in 15ml of $0.2ML^{-1}$ HCl solution and the aqueous solution of $ZnCl_2$ was added. After stirring the admixture for 1hour, the solvent was slowly evaporated by heating at 70^0C, while stirring gently. The catalyst was then dried at 120^0C for 10hours. The dried sample was thereafter calcined in a furnace at 500^0C for 4hours, and further reduced under hydrogen flow for another 4hours at 500^0C. This same procedure was repeated for five times to yield identical samples equivalent to 1.0wt% Zn/Al_2O_3 catalysts.

Development of Bimetallic Catalyst:

Varying weights of H_2PtCl_6 (0.1042, 0.2083, 0.3125, and 0.3750g) were dissolved in four beakers each containing 100ml of distilled water, and stirred properly to form aqueous solutions. Four of the earlier prepared Zn/Al_2O_3 catalysts (8g, 8g, 8g, and 7g) were added respectively to the aqueous solutions of H_2PtCl_6. After proper stirring, the admixtures were dried, calcined and reduced under hydrogen flow as enumerated for the preparation of monometallic catalysts. This resulted in four (4) different catalyst samples, each containing 1.0% Zn, but 0.5, 1.0, 1.5, and 2.0wt% of Pt, respectively.

3.4.2 Characterization of Catalysts

The textural properties (i.e specific surface area, pore volume, and pore size) were determined from Brunauer-Emmett-Teller (BET) method via N_2 adsorption using V-Sorb 2800P Surface Area and Porosimetry Analyzer at the National Research Institute for Chemical Technology (NARICT), Zaria. The X-ray diffraction (XRD) patterns were obtained using Empyreal PANalytical diffractometer employing Cu Kα radiation ($\lambda = 0.154$nm) at the National Geoscience Research Laboratories (NGRL), Kaduna. Scanning electron microscopy (SEM) imaging was conducted at the Department of Chemical Engineering, ABU, Zaria.

3.4.3 Catalysts' Performance Evaluations

In a typical run, about 0.20g of the catalyst sample was packed (loaded) halfway within a tubular reaction vessel, a 56cm long by 1.0cm internal diameter 'silica tube'. The schematic set-up is as shown in Fig 3.1. Glass-fibres were placed before and after the catalyst bed to homogenize the reactant mixture and temperature. Prior to any reaction, the reactor's temperature was steadily increased to the desired reaction temperature and held at that temperature.

n-octane in a flask was heated (to vaporize) and the vapor was channeled downstream into the reactor. The vapor outlet (the reformate) from the reaction zone was condensed as it passed through the condenser. The condensed reformate was collected as product. The procedure was repeated for five different reaction temperatures (430, 455, 480, 505, and 530^0C) for each of the catalyst samples developed. The constituents and compositions of the reformate obtained in each case was determined with the aid of a QP2010 PLUS GC-MS machine at NARICT Zaria.

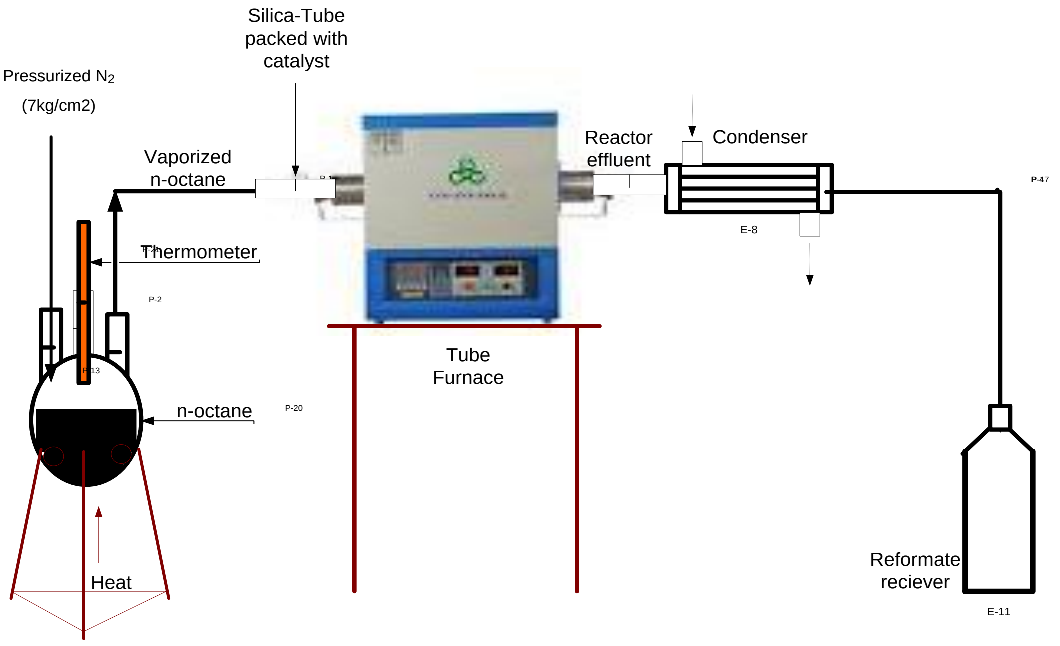


Figure 3.1: Schematic diagram for the laboratory set-up for n-octane reformation

CHAPTER FOUR

RESULTS AND DISCUSSION

The catalysts formulated are as follows: the catalyst support (gamma-alumina), Zn/Al_2O_3, 0.5%Pt-Zn/Al_2O_3, 1.0%Pt-Zn/Al_2O_3, 1.5%Pt-Zn/Al_2O_3, and 2.0%Pt-Zn/Al_2O_3 catalysts. Aside the support which contains no zinc, each of the other catalysts contains 1.0%wt of Zn. The results of all the analyses carried out are presented and discussed hereunder.

4.1 CATALYST CHARACTERIZATION

4.1.1 XRD Analysis

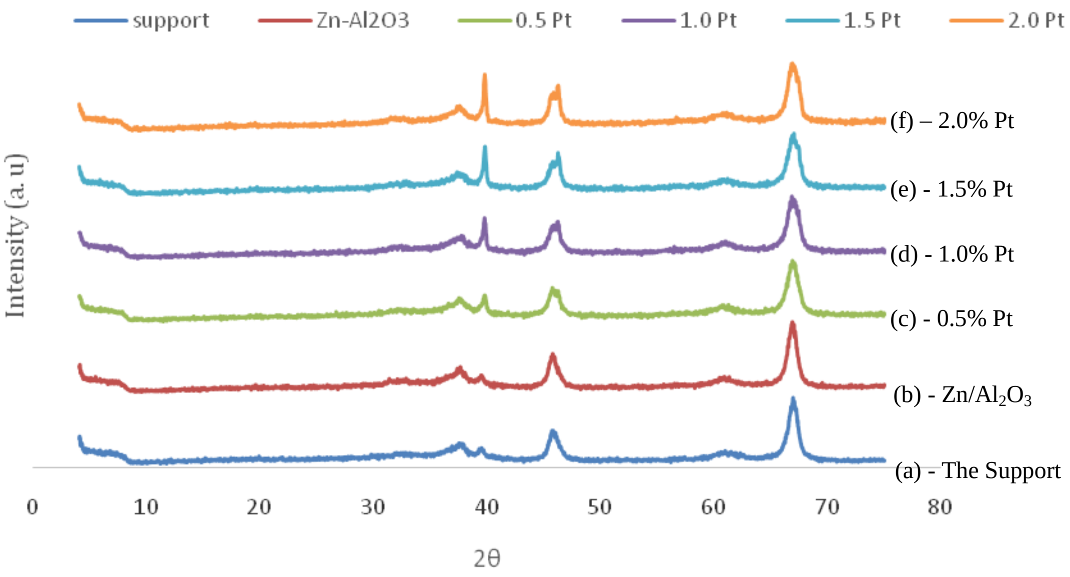


Figure 4.1: XRD patterns of the six developed catalysts

The XRD diffractograms obtained from Empyreal PANalytical Diffractometer for the catalysts (b,c,d,e,f) and the support (a) are as shown in Figure 4.1. Each of the catalysts in Figures 4.1: b, c, d, e, and f contains 1.0%wt Zn but 0%wt, 0.5%wt, 1.0%wt, 1.5%wt, and 2.0%wt of Pt, respectively.

The low intensity counts and the broad peaks that characterized the diffractographs of the support (γ-Al_2O_3) averred to the fact that the gamma-alumina is amorphous. The Zn/Al_2O_3 catalyst and the sets of Pt-Zn/Al_2O_3 catalysts have closely related bragg angles (2θs) with those of the support, but with different intensity counts.

The bragg angles (obtained in this work) for gamma-alumina exist at: 37, 39, 46, 60, and 66^0 (Fig. 4.1(a)), which conform with $2\theta=37.2^0\pm0.1^0$, $45.6^0\pm1^0$, and $66.9^0\pm1^0$ which are the XRD standard Bragg angles for gamma-alumina structure (with JCPDS reference no. 00-010-0425) in the International Centre for Diffraction Data (ICDD) database, (Rozita *et al*, 2010). The obtained result also agrees with those (37^0, 39^0, 46^0, 60^0, 67^0) cited from the works of Hosseini *et al* (2011), Mandana *et al* (2011), Ates (2011) and Bawa (2012).

The XRD diffractogram peaks for the Zn/Al_2O_3 catalyst appear to coincide with those of the support (due to the large weight proportion of the support compared to the doped zinc); but a little distinction however exist if closely observed. These Bragg angles: 37, 39, 60, and 66^0 for Zn/Al_2O_3 are same for values stored in the ICDD database for Zn metallic phase Zn(JCPDS PDF #00-004-0831), Lupan *et al* (2008).

In the present work, the XRD patterns for the Pt-Zn/Al_2O_3 catalysts (Fig 4.1 (c-f)) have Braggs angles (37^0, 40^0, 46^0, 67^0) which coincides with those of the support or the Zn/Al_2O_3 catalyst, except that platinum shows a distinct peak at 40^0 and 46^0. The steady rise in the peak narrowness and intensity at 40^0 indicates increase in the platinum content from 0.5% to 2.0%. At 46^0, the peaks of Pt-Zn/Al_2O_3 displayed characteristic trough and crest features which are absent in those of the support or Zn/Al_2O_3 catalyst. The works of Yasuharu *et al* (2005) also corroborated the fact of XRD pattern of platinum has bragg angles of 17^0, 40^0, 46^0, 67^0. Likewise, Gobara *et al* (2014) affirmed that 0.9%Pt/Al_2O_3 catalyst have Bragg angles of 39.8^0, 46.5^0 and 67.8^0 which are attributes of Pt metallic phase in accordance with the ICDD database: JCPDS 01-1190.

4.1.2 Catalysts' textural properties

Table 4.1: Textural properties of the catalysts

Sample	**Specific Surface Area (SSA) (m^2/g)**	**Pore Volume (cm^3/g)**	**Average Pore Size (nm)**
Acidified γ-alumina	50.93	0.0266	2.0864
Zn/Al_2O_3	54.73	0.0287	2.0977
0.5% Pt-Zn/Al_2O_3	77.65	0.0390	2.0107
1.0% Pt-Zn/Al_2O_3	55.42	0.0278	2.0078
1.5% Pt-Zn/Al_2O_3	79.40	0.0396	1.9956
2.0% Pt-Zn/Al_2O_3	43.94	0.0229	2.0832

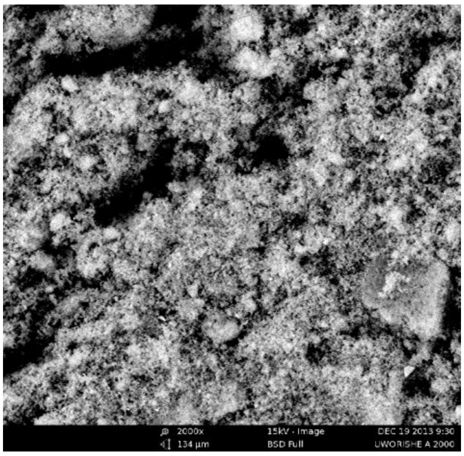
The specific surface area (BET), pore size, and pore volume were determined by N_2 adsorption using a V-Sorb 2800P Surface Area and Porosimetry Analyzer as presented in Table 4.1. The values of the pore sizes obtained are in the range of 2nm-2.10nm. This implies that they were all mesoporous (Luciene *et al*, 2012).

Doping the acidified support with zinc (thus forming a Zn/Al_2O_3 matrix) brought about significant increase in the support's textural properties; (SSA increased by 7.50%, pore volume increased by 7.90%, and pore size increased by 0.54%). These slight improvements in the surface morphology were evidents that a zinc aluminate ($ZnAl_2O_4$) surface-like spinel was formed (George *et al*, 1996). With additional doping with Pt, there was corresponding decrease in the average pore sizes with increase in the Pt content. This is an indication of progressive deposition of the Pt onto the supports' interior pore spaces. With increase in the content of Pt adsorbed onto the pore spaces, the pore sizes eventually decrease accordingly. As such, a strong interaction of Pt particles with the γ-alumina was suspected.

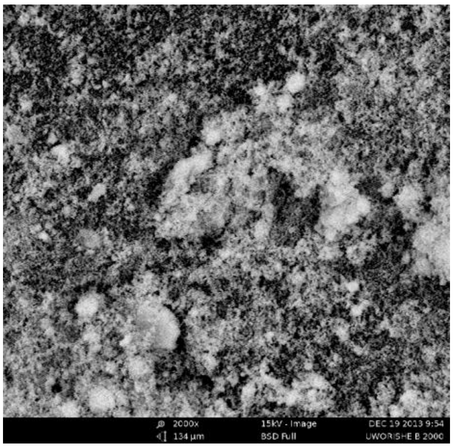
Change (increase or decrease) in SSA, does not indicate direct correlation with the change in the content of the doped active metal (Pt) on the support. Reason for such inconsistencies is unknown presently. Nonetheless, the SSA values fall within the range (15-300m^2/g) reported by Salahudeen (2012) for gamma-alumina.

4.1.3 Catalysts' Surface Morphology

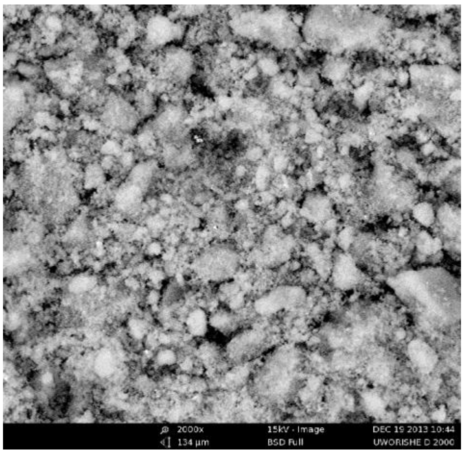
Plate I(a-f) shows the SEM images obtained for each of the catalysts' sample. Plate I(a) shows the image for the support (γ-alumina). One could easily observe uniformity in the crystal sizes and geometric distribution, indicating presence of identical crystals. The presence of few clusters of crystal particles in Plate I(b) shows evident of zinc particles. The population and the spread of the agglomerated particles increase with increase content of Pt on the Zn/Al_2O_3 matrix, Plate I(c-f). The spread or dispersion of these clustered nanoparticles were been enhanced by the zinc, (George *et al*, 1996). It is believed that use of transmission electron microscope (TEM) instead of the SEM will give a better resolution that will show clearer distinctions between the Zn and Pt crystallites.



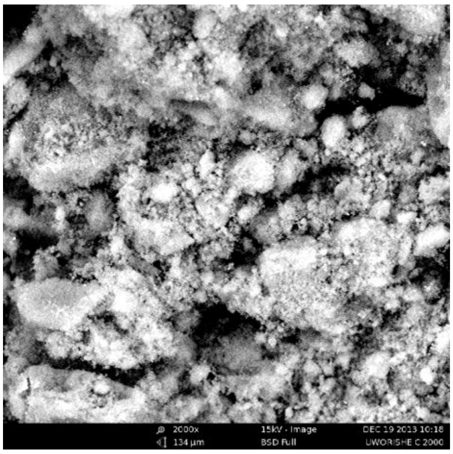
(a) The support (γ-alumina)



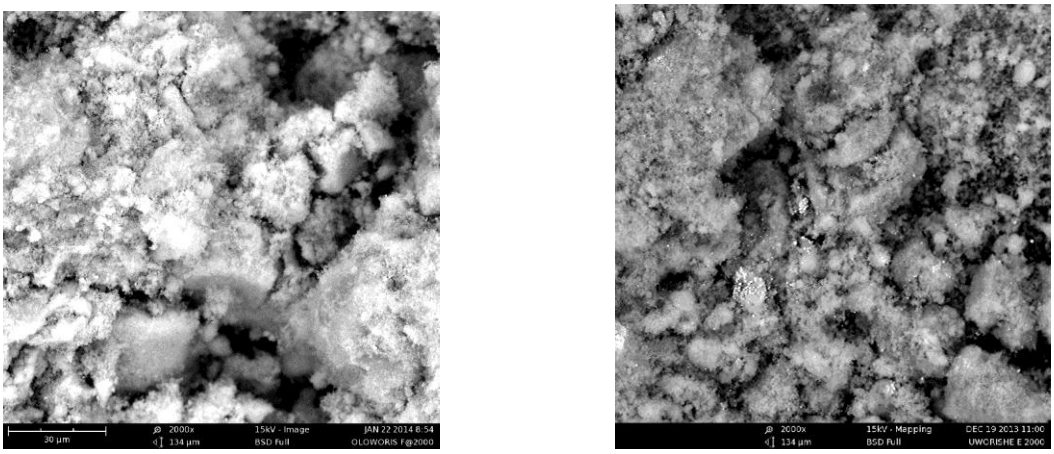
(b) Zn/Al_2O_3 catalyst



(c) 0.5% $Pt\text{-}Zn/Al_2O_3$ catalyst



(d) 1.0 $Pt\text{-}Zn/Al_2O_3$ catalyst



(e) 1.5% Pt-Zn/Al_2O_3 catalyst (f) 2.0% Pt-Zn/Al_2O_3 catalyst

Plate I(a-f): SEM images of the six developed catalysts samples

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4.2 CATALYSTS' PERFORMANCE EVALUATIONS

The catalyst performance evaluation was examined on the basis of catalyst's ability to enhance the yield of reformate from n-octane. The n-octane feed was pure (see Appendix B, Table A-1(i)). The assumed composition of the byproducts (i.e the dry gases) in the entire products was cited from the work of Karla (2009). The operating temperatures used ranges from 430^0C to 530^0C (under 7.0kg/cm^2 of pressure) for the various catalysts packed (Figure 4.3(a-f)).

n-octane feeds (F) $\xrightarrow{\text{(reforming)}}$ Products

Product = Sample collected + byproducts

byproducts = (H_2 + Off-gases + LPGs) = X

Sample collected = Unconverted n-octane (N) + reformate (R)

Hence, from the chromatograms of each sample analyzed, the area assigned to the unconverted n-octane was taken as N, while the total area assigned to all reformates was taken as R. Recall, X = 14.50wt% of the entire product, (Kalra, 2009).

Let:

Feed (n-octane) = F

Such that:

Products = $R + N + X$

Feed consumed: $f = F - N = X + R$

Thus, the percentage yield (Y_R) of reformates for each run/sample is:

$$Y_R = \frac{R}{n-octane\ \ consumed} \times 100\% = \left(\frac{R}{X+R}\right) \times 100\%$$

Where:

R = wt % of reformate

N = wt% of unconverted feed

X = wt % of the byproducts

4.2.1 Component Identification Method

4.2.1.1 *Qualitative analysis*

Generally chromatographic data is presented as a graph of detector response (y-axis) against retention time (x-axis), which is called a chromatogram. This provides a spectrum of peaks for a sample representing the analytes present in a sample eluting from the column at different times. Retention time was used to identify analytes under identical conditions. Also, the pattern of peaks (which was constant for a sample under constant conditions) was used to identify complex mixtures of analytes. The GC was incorporated to a Mass Spectrometer (i.e GC-MS), such that the MS identified the analytes represented by the peaks.

4.2.1.2 *Quantitative analysis*

Theoretically, the area under a peak is proportional to the amount of analyte present in the chromatogram. The area of the peak is proportional to the concentration of an analyte in the original sample. Concentration was obtained using a calibration curve created by finding the response for a series of concentrations of analyte, or by determining the relative response factor of an analyte. The relative response factor is the expected ratio of an analyte to an internal standard (or external standard) and was calculated by finding the response of a known amount of analyte and a constant amount of internal standard. The GC-MS system used, have computer software used to draw and integrate peaks, and thus match the obtained MS spectra to library spectra. Thus, an analytes present in a sample eluting from the column was named by match-making, and the most likely analyte's names were given (in order of probability; SI) in each spectrum. For instance, the spectrum (connoted by the GC-MS machine as Hit# 1) shown in Figure 4.3 is "Toluene"- which is the compound name with its isomers (each placed within the two double-dollar-sign).

Hit#:1 Entry:1224 Library:NIST05s.LIB
SI:92 Formula:C_7H_8 CAS:108-88-3 MolWeight:92 RetIndex:794

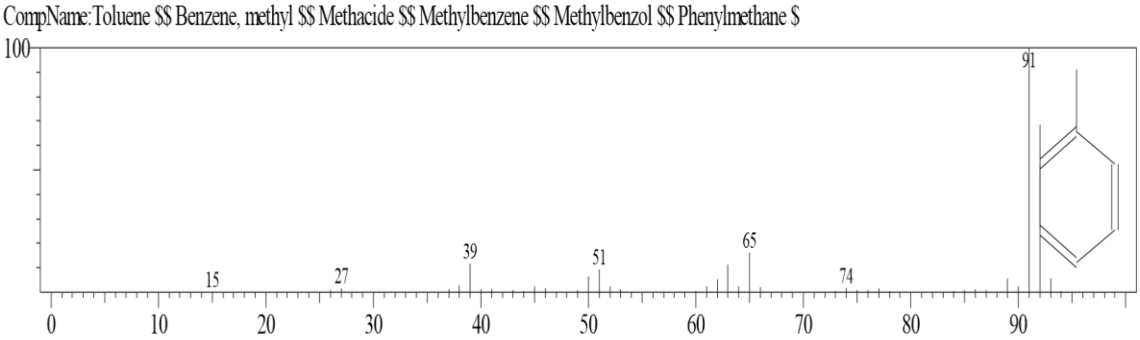

Figure 4.2: A Mass Spectrum.

4.2.2 Effects of Catalyst Loading

Reforming reactions take place when the reactor was packed with catalysts. No reaction occurs when the reactor was empty, thus reformate yields were zero in those cases; (see Appendices A and B).

4.2.2.1 *Reactor packed with the support*

Figure 4.3 (a) shows the yield pattern when the reactor was packed with the acidified porous support. A significant enhancement in the reformate yield with corresponding increases in the reactor's temperature could be noticed. This could be attributed to the following phenomena:

a. moderating the flow-rate of the n-octane across the reactor.

b. the heat from the furnace is well retained (conserved) by the support as the feed flow-pass, thus facilitating high possibility of isomerization.

c. the gamma-alumina, having been chlorinated, have very high potential to catalyze isomerization and cyclization reactions (55 ne *et al*, 2012).

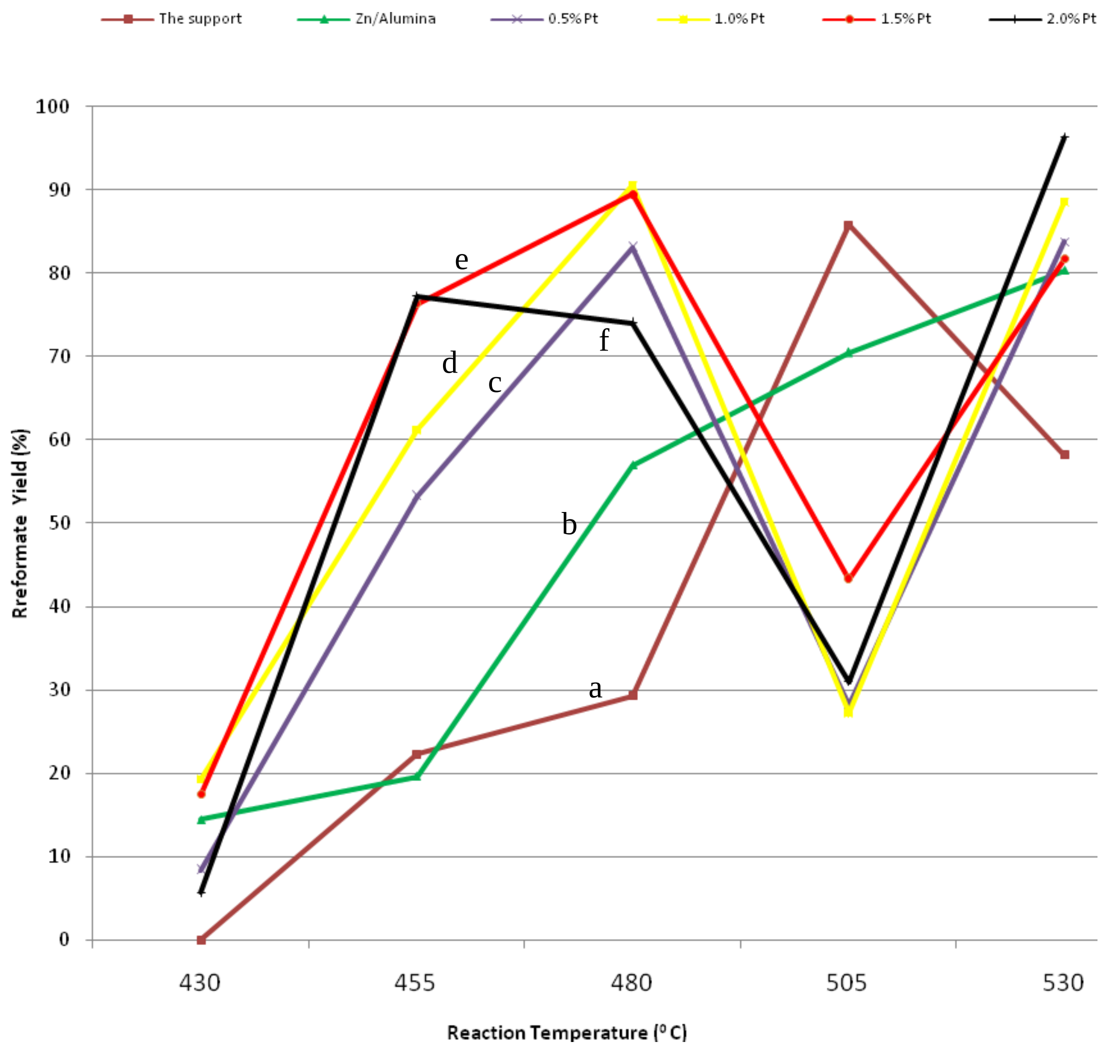

Figure 4.3 (a-f): Plots of Yield of reformate versus Temperature for the catalysts' packed reactors.

It is clear from Figure 4.3(a) that the yield of reformate increases with temperature, implying that the reactions were endothermic up-to 505^0C. Operating the support-packed reactor at 430^0C gives no yield due possibly to insufficient temperature (at such reactor's conditions). As temperature rose beyond 430^0C, there was progressive increase in yield with increase in temperature. At 455 and 480^0C, the support has good yield of reformate (57% & 63%) and moderate selectivity for aromatics of abou 56 % and 63%. The ability of the support to significantly enhance the production of aromatics arose from the fact that it (the support) was modified through halogenations and chlorination.

At 505^0C and 530^0C, the yield were 83% and 77% respectively, but less than half of the reformate compositions were aromatics; which does not attain the minimum of 70% aromatics required of a standard reformate; as specified by API (1994). These confirmed that the support (γ-alumina) has low selectivity for aromatics at 505^0C and 530^0C, but good selectivity for iso-paraffins. See Appendix A. Thus, the reformate got, in this instance, resulted mainly from the isomerization of n-octane (paraffinic feed), and possibly from cracked products. This observation is not unexpected in that the support has the potential to catalyze isomerization reaction (wherein iso-paraffins are majorly produced), whereas aromatics are mainly produced by dehydrocyclization reactions, which are largely promoted by an active metal, (Luciene *et al*, 2012). Beyond 505^0C, reformate yields decreases possibly due to over-cracking reactions leading to the generation of undesirable light gases as byproducts.

4.2.2.2 *Reactor Packed with Zn/Al_2O_3 Catalyst*

With the reactor packed with Zn/Al_2O_3 catalyst (Figure 4.3(b)), the yield of reformate increases steadily to attain 83% at 530^0C. It should be noted that a reformer that will have to run at temperature of 530^0C before attaining a reformate yield of 82% is virtually operating at its '*end-of-run'*, and will not be economically feasible as the catalyst will easily be prone to sintering due to operational severity. Nonetheless, the catalyst showed high selectivity for aromatics, but low selectivity for iso-paraffins within the five temperatures examined.

4.2.2.3 *Reactors Packed with Different Loading of Pt on the Zn/A_2O_3 Matrix*

The reformate yields for the reactors loaded with 0.5wt%, 1.0wt%, 1.5wt% and 2.0wt% Pt-Zn/Al_2O_3 catalysts were quite similar. For instance, with the reactor packed with 0.5% Pt-Zn/Al_2O_3 catalyst, Figure 4.3(c), the yield recorded at temperature of 430^0C was quite low; due to low operating temperature; resulting in incomplete reactions. Beyond 430^0C upto 480^0C, yield increases steadily and reached as high as 83% with large composition of aromatics in the reformates; this is because the dehydrocyclization of the paraffinic feed to aromatics requires severe process conditions, which the catalyst was able to initiate at such operating temperature. Similar conditions applied to all Pt doped catalysts.

For each of the four (0.5%, 1.0%, 1.5%, and 2.0% wt) Pt loadings (Fig 4.3 (c to f)), an obvious decrease in yield is observed at 505^0C. Reasons for such anomalous phenomena are not precisely known to us presently. Though, presumably, such erratic yield might be possibly due to presence of very few entrained ZnO in the catalyst. ZnO may results from small amount of zinc not forming zinc aluminate ($ZnAl_2O_4$) surface-like spinels. Thus, the ZnO becomes reduced to molten Zn at such temperatures, and can migrate onto Pt clusters or form PtZn alloys. George *et al* (1996) argued that these alloys are detrimental to the catalysts performance, as the alloy became unstable at elevated temperature; thus causing fluctuations in the reformate yields.

Operating the rig at temperature of 530^0C (Figure 4.3(c-f)) favours the dehydrocyclization of the paraffinic feed to aromatics, thus the rise in reformate yield. Such operating conditions, and the catalysts’ activeness were sufficient to provide the require severity of process parameters. Though, operating at such condition of temperature will compromise the life-span of the catalyst; due to sintering effects. Hence, most reformers are not designed to be operated at such high temperature despite the ostentatious yield.

4.2.2.4 *Summary of Catalysts Performance Evaluations*

Table 4.2 shows succinct details from Figures 4.3 (a-f) discussed earlier. It is an extract from Appendices A and B.

Table 4.2: Summary of the n-octane reforming conditions and products

S/N	Reactor packing	Max yield attained (%)	Temp range from min to max yield (^0C)	Quality of product
1	Chlorinated γ-Al_2O_3	83	455 - 505	< 64% of aromatics
2	Zn/Al_2O_3	83	430 - 530	≥ 73% aromatics
3	0.5% Pt-Zn/Al_2O_3	83	430 - 480	≥ 73% aromatics
4	1.0% Pt-Zn/Al_2O_3	84	430 - 480	≥ 73% aromatics
5	1.5% Pt-Zn/Al_2O_3	84	430 - 480	≥ 78% aromatics
6	2.0% Pt-Zn/Al_2O_3	85	430 - 530	≥ 82% aromatics
7	The n-octane feed			Purely paraffinic

Table 4.2 presents the relative aromatics fraction obtained from the different catalysts tested. Of important is the fact that introduction of Pt even at low concentration of 0.5 wt% was sufficient to reduce the optimum operating temperature to 480^0C compared to 530^0C required for the monometallic catalyst to produce the same effect in terms of aromatics composition in the reformate. Equally obvious from the table is the role of the metals in yielding acceptable reformate with aromatics composition greater than 70% as approved by API (1994) when compared to that of sole acidified support.

4.2.3 Selectivity

The selectivity of all the catalysts (with the exemption of the support) for iso-paraffins were relatively low (see Appendice A, Table A-3 for the raw data). The support alone had significant selectivity of about 35% and 47% at 505^{0}C and 530^{0}C, respectively. This is because the acidified support was able to catalyze isomerization reaction wherein iso-paraffins are largely produced (See Fig 4.4).

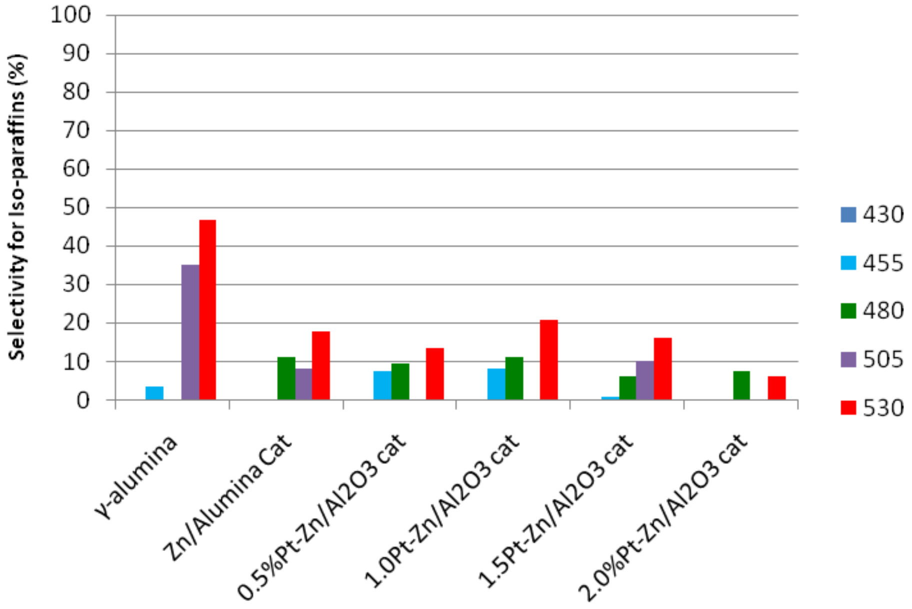

Fig. 4.4: Selectivity for iso-paraffins for each catalyst

The selectivity of all the catalysts (with the exemption of the support) for aromatics was quite impressive; ranging from 25% to 82%, (see Fig 4.5). The least selectivity for each catalyst was recorded at 430^{0}C, while peak values were recorded at 455 and 480^{0}C; except for Zn/Al_2O_3 catalyst. For the Zn/Al_2O_3 catalyst, selectivity raises steady with temperature to attain peak value of 72% at 505^{0}C and thereafter declined to 65% at 530^{0}C. For the support, the selectivity ranges from 31% to 63% within 455 to 530^{0}C with no yield of reformate at 430^{0}C.

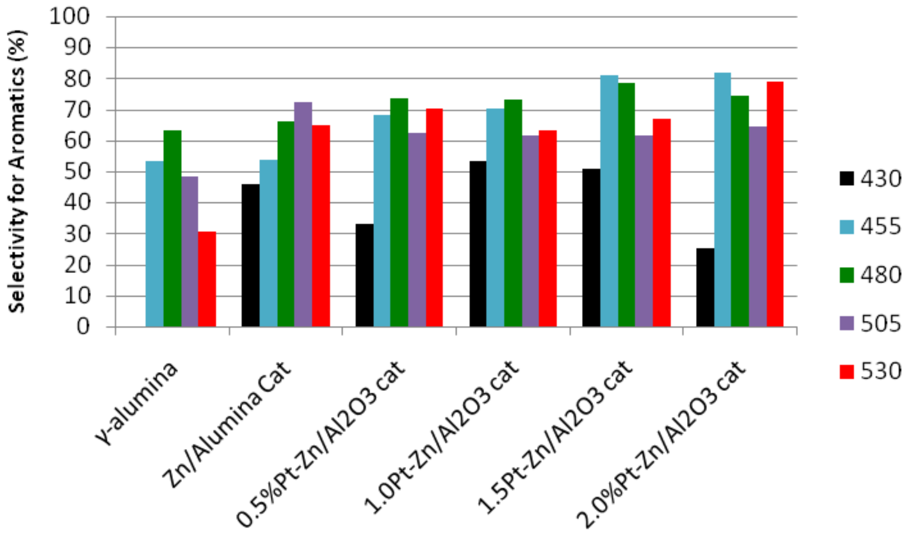

Fig. 4.5: Selectivity for aromatics for all the catalysts

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

Reforming catalysts have been developed by anchoring catalytically active metals on alumina matrix in this investigation, wherein the following conclusions could be drawn from the work carried out:

1. Platinum and zinc were both found to be active in the reformation tests conducted despite the fact that the original reason of its inclusion (Zn) was to enhance Pt dispersion on the support. Also, gamma-alumina was found to be a suitable support matrix due to its accessible surface area and porosity. These assertions were justified based on the ability of the individual catalyst to catalyze n-octane reforming.
2. It was found that the Bragg angles for gamma-alumina and Zn/Al_2O_3 catalyst both exit at 37, 39, 46, and 66^0, and those for $Pt\text{-}Zn/Al_2O_3$ catalyst exist at 37, 40, 46, and 67^0. The similarities in the bulk morphology of the characterized catalysts were attributed to the high weight percent (greater than 95%) of the support (γ-alumina) that was common to all the catalyst.
3. Verification of the extent of metal dispersion may be made more explicit if TEM technique is adopted instead of the SEM technique used herein.
4. The change in the textural properties of the catalysts corresponds with the increases in the doped active metal(s) from 0% to 0.50% of Pt. Thereafter, changes in the specific surface area and the pore volume became erratic. These properties that were keenly examined are fairly similar with those reported in literatures.

5. The catalytic performance of the prepared catalysts for n-octane reforming revealed higher reformate yield for the Pt containing catalysts relative to the non-platinum catalysts. Furthermore, with Pt, optimum yield of reformate was attainable at lesser severe reforming temperature (430-480^{0}C) as compared to 430-530^{0}C required for the non-Pt catalysts. This will eventually translates to lesser running cost in comparism to the non-platinum catalysts.
6. The major effect of the catalytic processes on the n-octane (naphtha) feed was the improvement in octane rating, thus making the products suitable for gasoline blending, or as petrochemical feedstocks.

5.2 RECOMMENDATIONS

1. For proper accountability for all the products of reforming system, it is recommended that a direct on-line analyzer be incorporated to the rig (the lab set-up). This will make it possible for the byproducts, and/or volatile gases (LPGs, off-gases and H_2) to be precisely accounted-for.

2. Aside the impregnation techniques used herein, other catalyst preparation methods (adsorption from solution, co-precipitation, or deposition) should as well be adopted for preparing same set of catalysts. The performances of such catalysts for naphtha reforming should be evaluated so as to examine the effects of preparation methods on performance.

3. Besides the n-octane (C_8) used in this work, other model feeds such as C_6, C_7, C_9, C_{10}, C_{11}, and C_{12} should be used as feed to establish the performance of the developed catalysts on the entire heavy naphtha fractions.

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APPENDIX A

CATALYSTS PERFORMANCE EVALUATIONS

Tables A-1 below give the summarized GC-MS results of the reformate samples, with the feed (the n-octane).

Table A-1(i): Summarized GC-MS results for the feed and for the reformates got from the empty reactor.

Rxn Temp (^oC)	Composition of the reformate as analyzed with a GC-MS Machine					
		Percentage of chromatogram area assigned to component				
	Sample compositions	**Individual (%)**	**Unconverted n-octane**	**Total Iso-paraffins (%)**	**Total Aromatics (%)**	**Yield of reformate (%)**
The Feed						
	n-octane	100	100	-	-	-
Empty Reactor						
430	n-octane	100	100	-	-	0
455	n-octane	100	100	-	-	0
480	n-octane	100	100	-	-	0
505	n-octane	100	100	-	-	0
530	n-octane	100	100	-	-	0

Table A-1 (ii): Summarized GC-MS results for reactor packed with Gamma-Alumina

Rxn Temp (^{o}C)	Composition of the reformate as analyzed with a GC-MS Machine					
		Percentage of chromatogram area assigned to component				
	Sample compositions	**Individual (%)**	**Unconverted n-octane**	**Total Iso-paraffins (%)**	**Total Aromatics (%)**	**Yield of reformate (%)**
430	n-octane	100	100	-	-	0
455	Methylbenzene	7.79	77.69	1.33	20.99	22.32
	n-octane	77.69				
	1,4-Dimethylbenzene	9.57				
	Isopropylbenzene	3.63				
	2,3-Dimethylpentane	1.33				
480	Methylbenzene	12.27	70.69	-	29.31	29.31
	n-octane	70.69				
	Phenylethane	11.33				
	n-Nonanophenone	5.72				
505	1-Nitro-2-methylpropane					
	Methylbenzene	0.89	14.16	36.09	49.74	85.83

	n-octane	1.29				
	2-Methylbutane	14.16				
	Ethylbenzol	1.38				
	Pentanophenone	2.99				
	Methylbutanoate	1.90				
	Tetrahydro-2-furanymethylchloroacetate	33.82				
		43.56				
530	2,4-Dimethylpentane	8.19	41.97	35.02	23.0	58.20
	Cyclohepta-1,3,5-triene	9.69				
	n-octane	41.97				
	2-Methylhexane	7.26				
	Ethylbenzol	15.30				
	2-Methylbutane	3.67				
	Isopropylbenzene	7.70				
	2,3-Dimethylbutane	6.21				

Table A-1 (iii): Summarized GC-MS results for reactor packed with Zn/Al_2O_3 Catalyst

Rxn Temp	

Composition of the reformate as analyzed with a GC-MS Machine

		Percentage of chromatogram area assigned to component				
(°C)	**Sample compositions**	**Individual (%)**	**Unconverted n-octane**	**Total Iso-paraffins (%)**	**Total Aromatics (%)**	**Yield of reformate (%)**
430	Methylbenzene	4.36	85.52	-	14.48	14.48
	n-octane	85.52				
	Ethylbenzol	6.86				
	Dibenzoyl	3.25				
455	Methylbenzene	3.92	80.37	-	19.63	19.63
	n-octane	80.37				
	1, 4-Dimethylbenzene	7.90				
	o-Ethyltoluene	3.44				
	1,2,3-Trimethylbenzene	4.37				
480	2,2,3-Trimethylbutane	3.76	43.02	8.19	48.79	56.98
	Methylbenzene	8.09				
	n-octane	43.02				
	2,4-Dimethylpentane	4.43				
	1,4-Dimethylbenzene	20.03				
	Benzene	6.02				
	Benzoyl methide	2.57				
	2-Phenylpropane	12.08				
505	2,2,3-Trimethylbutane	4.05	29.51	7.07	63.42	70.49
	Methylbenzene	20.80				
	n-octane	29.51				
	2,3-Dimethylpentane	3.02				
	1,4-Dimethylbenzene	21.48				
	Phenylethane	5.43				
	2-Phenylpropane	15.72				

530	2-Methylheptane	7.41	19.65	17.16	63.19	80.34
	2,2,3-Trimethylbutane	7.27				
	n-octane	19.65				
	1,4-Dimethylbenzene	18.26				
	2,4-Dimethylpentane	2.48				
	Phenylethane	5.97				
	Isopropylbenzene	16.34				
	1,2,3-Trimethylbenzene	12.64				
	m-Propyltoluene	3.29				
	Butylbenzene	2.38				
	Dimethylethylbenzene	3.42				
	4-(Benzyloxy)phenyl -2-methylbenzoate	0.88				

Table A-1 (iv): Summarized GC-MS results for reactor packed with 0.50% Pt-Zn/Al_2O_3

Rxn Temp (^{o}C)	Composition of the reformate as analyzed with a GC-MS Machine					
		Percentage of chromatogram area assigned to component				
	Sample compositions	**Individual (%)**	**Unconverted n-octane**	**Total Iso-paraffins (%)**	**Total Aromatics (%)**	**Yield of reformate (%)**
430	Methylbenzene	3.85	91.63	-	8.37	8.38

	n-octane	91.63				
	Ethylbenzol	3.18				
	2-Phenylpropane	1.35				
455	2,4-Dimethylhexane	3.14	46.73	5.34	47.93	53.27
	Methylbenzene	10.43				
	n-octane	46.73				
	2-Methyloctane	2.20				
	Ethylbenzene	3.50				
	1,4-Dimethylbenzene	15.67				
	Ethylbenzol	4.90				
	Isopropylbenzene	5.93				
	1,2,3-Trimethylbenzene	7.50				
480	3-Ethyl-2-methylhexane	4.15	16.95	9.58	73.47	83.07
	Methylbenzene	10.50				
	n-octane	16.95				
	2,3,4-Trimethylhexane	3.58				
	1,4-Dimethylbenzene	27.72				
	2,4-Dimethylpentane	1.85				
	Propylbenzene	3.01				
	o-Ethyltoluene	9.53				
	2-Phenylpropane (Cumene)	5.55				
	1,2,3-Trimethylbenzene	11.66				
	2-Phenylbutane	2.33				
	Dimethylethylbenzene	1.23				
	1,4-Diethylbenzene	1.21				
	Cyclopentacycloheptene	0.75				
505	Methylbenzene	7.19	71.81	-	28.19	28.19
	n-octane	71.81				
	1,4-Dimethylbenzene	11.55				
	Cumene	4.15				

	Isopropylbenzene	5.30				
530	2-Methylbutane	4.73	13.28	13.66	73.06	86.66
	2,4-Dimethylpentane	4.29				
	Methylbenzene	11.58				
	n-octane	13.28				
	3-Ethylhexane	4.64				
	1,4-Dimethylbenzene	24.22				
	Ethylbenzol	7.52				
	Neopentylbenzene	2.96				
	Cumene	10.07				
	1,2,3-Trimethylbenzene	12.31				
	1-Phenyl-1-pentanone	1.26				
	Other Aromatics	3.15				

Table A-1 (v): Summarized GC-MS results for reactor packed with 1.0% Pt-Zn/Al_2O_3

Rxn Temp (^{o}C)	Composition of the reformate as analyzed with a GC-MS Machine					
		Percentage of chromatogram area assigned to component				
	Sample compositions	**Individual (%)**	**Unconverted n-octane**	**Total Iso-paraffins (%)**	**Total Aromatics (%)**	**Yield of reformate (%)**
430	Methylbenzene	10.99	80.70	-	19.30	19.30
	n-octane	80.70				
	1,4-Dimethylbenzene	5.15				
	1,2,3-Trimethylbenzene	3.16				

455	2,4-Dimethylpentane	3.62	38.84	6.39	54.77	61.19
	Methylbenzene	5.91				
	n-octane	38.84				
	2,6-Dimethylheptane	2.77				
	(3,3-Dimethylbutyl)benzene	5.89				
	1,4-Dimethylbenzene	18.38				
	Phenylethane	6.59				
	m-Ethyltoluene	4.61				
	1,2,3-Trimethylbenzene	13.39				
480	2-Methylheptane	4.50	9.42	11.98	78.60	90.58
	3-Methylheptane	4.58				
	Methylbenzene	23.50				
	n-octane	9.42				
	2,3,3-Trimethylpentane	2.90				
	Phenylethane	6.77				
	1,4-Dimethylbenzene	21.37				
	1,2-Dimethylbenzene	6.86				
	o-Ethyltoluene	7.18				
	2-Phenylpropane	3.17				
	1,2,3-Trimethylbenzene	9.76				
505	Methylbenzene	11.30	72.77	-	27.23	27.23
	n-octane	72.77				
	1,4-Dimethylbenzene	10.97				
	Cumene	4.96				
530	2-Methylheptane	6.59	11.42	21.74	66.83	88.57
	2,4-Dimethylpentane	6.17				
	Methylbenzene	18.37				
	n-octane	11.42				
	2,2,4-Trimethylpentane	1.74				
	2,3,4-Trimethylhexane	5.28				
	Phenylethane	6.66				

	1,2-Dimethylbenzene	17.11				
	2,4-Dimethylhexane	1.96				
	Mexiletine	5.32				
	2-Phenylpropane	6.53				
	1,2,4-Trimethylbenzene	2.49				
	1,2,3-Trimethylbenzene	8.01				
	Hydratropaldehyde	2.34				

Table A-1 (vi): Summarized GC-MS results for reactor packed with 1.5% Pt-Zn/Al$_2$O$_3$

430	Methylbenzene	7.40	82.52	-	17.48	17.48
	n-octane	82.52				
	1,2-Dimethylbenzene	5.82				
	o-Ethyltoluene	1.96				
	1,2,3-Trimethylbenzene	2.30				
455	n-octane	16.54	23.65	0.69	75.66	76.35
	1,2-Dimethylbenzene	2.91				
	2,7-Dimethyloctane	0.69				
	Phenylethane	1.41				
	Propylbenzene	2.99				
	m-Ethyltoluene	8.21				
	n-Decane	1.70				
	1,2,3-Trimethylbenzene	16.14				
	m-Propyltoluene	8.84				
	o-Isopropyltoluene	6.61				
	2-Phenylbutane	2.06				
	o-Isopropyltoluene	7.50				

	1,7-Octadiyne 4-Phenyl-2-butene 2,3-Dimethyl-2-phenylbutane Cyclopentacycloheptene 1-Methylnaphthalene	5.41 6.05 1.24 8.38 3.31				
480	3-Methylheptane Methylbenzene n-octane 2,3-Dimethylpentane (3,3-Dimethylbutyl) benzene 1,4-Dimethylbenzene Phenylethane Propylbenzene o-Ethyltoluene 1,2,3-Trimethylbenzene 1,2,4-Trimethylbenzene 2-Phenylbutane Butylbenzene Dimethylethylbenzene	3.64 24.32 10.53 2.38 6.34 21.51 7.01 2.31 7.61 8.79 1.37 1.79 1.37 1.02	10.53	6.02	83.45	89.47
505	3-Methylheptane Methylbenzene n-octane 2,5-Dimethylheptane 1,2-Dimethylbenzene Dimethylfulvene 1,2,4-Trimethylbenzene 1,2,3-Trimethylbenzene	2.37 10.39 56.73 3.73 12.48 3.90 4.52 5.87	56.73	6.10	37.17	43.26
530	2,4-Dimethylpentane Methylbenzene n-octane	7.30 19.06 18.25	18.25	15.80	65.95	81.75

	1,1,2-Trimethylethane	5.21				
	3-Methyloctane	3.29				
	1,4-Dimethylbenzene	19.50				
	Dimethylfulvene	5.83				
	Cumene	8.85				
	1,2,4-Trimethylbenzene	9.89				
	(1,3-Dimethylbutyl) benzene	2.83				

Table A-1 (vii): Summarized GC-MS results for reactor packed with 2.0% Pt-Zn/Al_2O_3

430	Methylbenzene	3.39	94.27	-	5.73	5.73
	n-octane	94.27				
	1,4-Xylene	2.34				
455	n-octane	22.74	22.74	-	77.26	77.26
	2-Phenylpropane	7.55				
	2-Phenylbutane	4.30				
	o-Isopropyltoluene	12.6416.07				
	Dimethylethylbenzene	3.63				
	2,8-Decadiyne	33.06				
	Other Aromatics					
480	3-Methylheptane	6.39	25.97	6.39	67.64	74.02
	Methylbenzene	15.58				
	n-octane	25.97				
	Ethylbenzol	6.37				
	1,4-Dimethylbenzene	19.98				
	o-Ethyltoluene	8.41				
	1,2,3-Trimethylbenzene	10.90				
	2-Phenylpropane	1.78				

	m-Propyltoluene Dimethylethylbenzene Cyclopentacycloheptene	1.65 1.69 1.27				
505	Methylbenzene n-octane Ethylbenzol 1,4-Dimethylbenzene o-Ethyltoluene 1,2,3-Trimethylbenzene	7.56 69.04 2.56 10.93 4.33 5.58	69.04	-	30.96	30.96
530	2-Methylheptane 3-Methylheptane n-octane 2,5-Dimethylheptane Phenylethane 1,4-Dimethylbenzene Propylbenzene o-Ethyltoluene 1,2,3-Trimethylbenzene 2-Phenylbutane o-Isopropyltoluene Other Aromatics	1.13 1.17 3.66 4.73 14.15 5.73 5.60 16.60 22.42 6.98 7.83 10.01	3.66	7.03	89.31	96.34

Tables A-2 (i-vi) are extensions of Tables A-1(i-vi); each with an additional column containing the weight percentage of the Dry Volatile Gases (the byproducts) which could not be captured along with the collected samples. The uniform weight percent (14.5wt%) assigned to the dry gases was referenced from Kalra (2009). Thus, the actual products captured/collected (isoparaffins, aromatics, with the unconverted n-octane) were taken (converted) to be 85.5% of the total products (dry volatile gases inclusive). The values in brackets, in Table A-2, were the raw data extracted from the GC-MS Results, while the values directly above them were the converted values having included the dry gases in the products’ compositions.

Table A-2: Estimated Products Composition

Table A-2(i): Summarized GC-MS results for the feed and for the reformates got from gamma-alumina packed reactor.

Rxn Temp (°C)	Composition of the products inclusive of the volatile gases							
		Percentage assigned to component						
		Individ-ual (%)	**Total Paraffins (n-octa) (%)**	**Total Iso-paraffins (%)**	**Total Aromatics (%)**	**Net reformate Product**	**Dry volatile gases= X**	**Yield of reformate (%)**
The Feed								
	n-octane	100	100	-	-	0	0	-
Reactor Packed Gamma-Alumina								
430	n-octane	100	85.5	-	-	0	14.50	0
455	Methylbenzene n-octane 1,4-Dimethylbenzene Isopropylbenzene 2,3-Dimethylpentane	7.79 77.69 9.57 3.63 1.33	66.42 (77.69)	1.14 (1.33)	17.95 (20.99)	19.09	14.50	56.83
480	Methylbenzene n-octane Phenylethane n-Nonanophenone	12.27 70.69 11.33 5.72	60.44 (70.69)	-	25.06 (29.31)	25.06	14.50	63.34
505	1-Nitro-2-methylpropane Methylbenzene n-octane 2-Methylbutane Ethylbenzol Pentanophenone Methylbutanoate Tetrahydro-2-	0.89 1.29 14.16 1.38 2.99 1.90 33.82	12.11 (14.16)	30.86 (36.09)	42.53 (49.74)	73.39	14.50	83.50

	furanymethylchloroacetate	43.56						
530	2,4-Dimethylpentane Cyclohepta-1,3,5-triene n-octane 2-Methylhexane Ethylbenzol 2-Methylbutane Isopropylbenzene 2,3-Dimethylbutane	8.19 9.69 41.97 7.26 15.30 3.67 7.70 6.21	35.88 (41.97)	29.94 (35.02)	19.67 (23.0)	49.61	14.50	77.23

Table A-2(ii): Summarized GC-MS Results for the Reactor packed with Zn/Al_2O_3 Catalyst.

430	Methylbenzene n-octane Ethylbenzol Dibenzoyl	4.36 85.52 6.86 3.25	73.12 (85.52)	-	12.37 (14.47)	12.37	14.50	46.04
455	Methylbenzene n-octane 1, 4-Dimethylbenzene o-Ethyltoluene 1,2,3-Trimethylbenzene	3.92 80.37 7.90 3.44 4.37	68.72 (80.37)	-	16.78 (19.63)	16.37	14.50	53.03
480	2,2,3-Trimethylbutane Methylbenzene	3.76 8.09	36.78 (43.02)	7.00 (8.19)	41.72 (48.79)	48.72	14.50	77.06

	n-octane	43.02						
	2,4-Dimethylpentane	4.43						
	1,4-Dimethylbenzene	20.03						
	Benzene	6.02						
	Benzoyl methide	2.57						
	2-Phenylpropane	12.08						
505	2,2,3-Trimethylbutane	4.05	25.23	6.04	54.22	60.26	14.50	80.60
	Methylbenzene	20.80	(29.51)	(7.07)	(63.42)			
	n-octane	29.51						
	2,3-Dimethylpentane	3.02						
	1,4-Dimethylbenzene	21.48						
	Phenylethane	5.43						
	2-Phenylpropane	15.72						
530	2-Methylheptane	7.41	16.80	14.67	54.13	68.70	14.50	82.57
	2,2,3-Trimethylbutane	7.27	(19.65)	(17.16)	(63.19)			
	n-octane	19.65						
	1,4-Dimethylbenzene	18.26						
	2,4-Dimethylpentane	2.48						
	Phenylethane	5.97						
	Isopropylbenzene	16.34						
	1,2,3-Trimethylbenzene	12.64						
	m-Propyltoluene	3.29						
	Butylbenzene	2.38						
	Dimethylethylbenzene	3.42						
	4-(Benzyloxy)phenyl -2-methylbenzoate	0.88						

Table A-2(iii): Summarized GC-MS results for the reactor packed with 0.50% Pt-Zn/Al_2O_3 Catalyst.

430	Methylbenzene n-octane Ethylbenzol 2-Phenylpropane	3.85 91.63 3.18 1.35	78.34 (91.63)	 -	7.16 (8.37)	7.16	14.50	33.06
455	2,4-Dimethylhexane Methylbenzene n-octane 2-Methyloctane Ethylbenzene 1,4-Dimethylbenzene Ethylbenzol Isopropylbenzene 1,2,3-Trimethylbenzene	3.14 10.43 46.73 2.20 3.50 15.67 4.90 5.93 7.50	39.95 (46.73)	4.57 (5.34)	40.98 (47.93)	45.55	14.50	75.85
480	3-Ethyl-2-methylhexane Methylbenzene n-octane 2,3,4-Trimethylhexane 1,4-Dimethylbenzene 2,4-Dimethylpentane Propylbenzene o-Ethyltoluene 2-Phenylpropane (Cumene) 1,2,3-Trimethylbenzene	4.15 10.50 16.95 3.58 27.72 1.85 3.01 9.53 5.55 11.66	14.49 (16.95)	8.19 (9.58)	62.82 (73.47)	71.01	14.50	83.04

	2-Phenylbutane	2.33						
	Dimethylethylbenzene	1.23						
	1,4-Diethylbenzene	1.21						
	Cyclopentacycloheptene	0.75						
505	Methylbenzene	7.19	61.40	-	24.10	24.10	14.50	62.44
	n-octane	71.81	(71.81)		(28.19)			
	1,4-Dimethylbenzene	11.55						
	Cumene	4.15						
	Isopropylbenzene	5.30						
530	2-Methylbutane	4.73	11.35	11.68	62.47	74.15	14.50	83.64
	2,4-Dimethylpentane	4.29	(13.28)	(13.66)	(73.06)			
	Methylbenzene	11.58						
	n-octane	13.28						
	3-Ethylhexane	4.64						
	1,4-Dimethylbenzene	24.22						
	Ethylbenzol	7.52						
	Neopentylbenzene	2.96						
	Cumene	10.07						
	1,2,3-Trimethylbenzene	12.31						
	1-Phenyl-1-pentanone	1.26						
	Other Aromatics	3.15						

Table A-2(iv): Summarized GC-MS results for the reactor packed with 1.0% Pt-Zn/Al_2O_3 Catalyst.

430	Methylbenzene	10.99	69.00		16.50	16.50	14.50	53.23
	n-octane	80.70	(80.70)	-	(19.30)			
	1,4-Dimethylbenzene	5.15						
	1,2,3-Trimethylbenzene	3.16						
455	2,4-Dimethylpentane	3.62	33.21	5.46	46.82	52.29	14.50	78.29
	Methylbenzene	5.91	(38.84)	(6.39)	(54.77)			
	n-octane	38.84						
	2,6-Dimethylheptane	2.77						
	(3,3-Dimethylbutyl)benzene	5.89						
	1,4-Dimethylbenzene	18.38						
	Phenylethane	6.59						
	m-Ethyltoluene	4.61						
	1,2,3-Trimethylbenzene	13.39						
480	2-Methylheptane	4.50	8.05	10.24	67.20	77.44	14.50	84.23
	3-Methylheptane	4.58	(9.42)	(11.98)	(78.60)			
	Methylbenzene	23.50						
	n-octane	9.42						
	2,3,3-Trimethylpentane	2.90						
	Phenylethane	6.77						
	1,4-Dimethylbenzene	21.37						
	1,2-Dimethylbenzene	6.86						
	o-Ethyltoluene	7.18						
	2-Phenylpropane	3.17						
	1,2,3-Trimethylbenzene	9.76						
505	Methylbenzene	11.30	62.22		23.28	23.28	14.50	61.62
	n-octane	72.77	(72.77)	-	(27.23)			
	1,4-Dimethylbenzene	10.97						
	Cumene	4.96						
530	2-Methylheptane	6.59	9.76	18.59	57.15	75.74	14.50	83.93
	2,4-Dimethylpentane	6.17	(11.42)	(21.74)	(66.84)			
	Methylbenzene	18.37						

	n-octane	11.42						
	2,2,4-Trimethylpentane	1.74						
	2,3,4-Trimethylhexane	5.28						
	Phenylethane	6.66						
	1,2-Dimethylbenzene	17.11						
	2,4-Dimethylhexane	1.96						
	Mexiletine	5.32						
	2-Phenylpropane	6.53						
	1,2,4-Trimethylbenzene	2.49						
	1,2,3-Trimethylbenzene	8.01						
	Hydratropaldehyde	2.34						

Table A-2(v): Summarized GC-MS results for the reactor packed with 1.5% Pt-Zn/Al_2O_3 Catalyst.

430	Methylbenzene	7.40	70.55		14.95	14.95	14.50	50.76
	n-octane	82.52	(82.52)	-	(17.48)			
	1,2-Dimethylbenzene	5.82						
	o-Ethyltoluene	1.96						
	1,2,3-Trimethylbenzene	2.30						
455	n-octane	16.54	20.22	0.59	64.69	65.28	14.50	81.83
	1,2-Dimethylbenzene	2.91	(23.65)	(0.69)	(75.66)			
	2,7-Dimethyloctane	0.69						
	Phenylethane	1.41						
	Propylbenzene	2.99						

	m-Ethyltoluene	8.21						
	n-Decane	1.70						
	1,2,3-Trimethylbenzene	16.14						
	m-Propyltoluene	8.84						
	o-Isopropyltoluene	6.61						
	2-Phenylbutane	2.06						
	o-Isopropyltoluene	7.50						
	1,7-Octadiyne	5.41						
	4-Phenyl-2-butene	6.05						
	2,3-Dimethyl-2-phenylbutane	1.24						
	Cyclopentacycloheptene	8.38						
	1-Methylnaphthalene	3.31						
480	3-Methylheptane	3.64	9.00	5.15	71.35	76.50	14.50	84.06
	Methylbenzene	24.32	(10.53)	(6.02)	(83.45)			
	n-octane	10.53						
	2,3-Dimethylpentane	2.38						
	(3,3-Dimethylbutyl)benzene	6.34						
	1,4-Dimethylbenzene	21.51						
	Phenylethane	7.01						
	Propylbenzene	2.31						
	o-Ethyltoluene	7.61						
	1,2,3-Trimethylbenzene	8.79						
	1,2,4-Trimethylbenzene	1.37						
	2-Phenylbutane	1.79						
	Butylbenzene	1.37						
	Dimethylethylbenzene	1.02						
505	3-Methylheptane	2.37	48.50	5.22	31.78	37.00	14.50	71.85
	Methylbenzene	10.39	(56.73)	(6.10)	(37.17)			
	n-octane	56.73						
	2,5-Dimethylheptane	3.73						
	1,2-Dimethylbenzene	12.48						

	Dimethylfulvene	3.90						
	1,2,4-Trimethylbenzene	4.52						
	1,2,3-Trimethylbenzene	5.87						
530	2,4-Dimethylpentane	7.30	15.60	13.51	56.39	69.90	14.50	82.82
	Methylbenzene	19.06	(18.25)	(15.80)	(65.95)			
	n-octane	18.25						
	1,1,2-Trimethylethane	5.21						
	3-Methyloctane	3.29						
	1,4-Dimethylbenzene	19.50						
	Dimethylfulvene	5.83						
	Cumene	8.85						
	1,2,4-Trimethylbenzene	9.89						
	(1,3-Dimethylbutyl)benzene	2.83						

Table A-2(vi): Summarized GC-MS results for the reactor packed with 2.0% Pt-Zn/Al_2O_3 Catalyst.

430	Methylbenzene	3.39	80.60		4.90	4.90	14.50	25.26
	n-octane	94.27	(94.27)	-	(5.73)			
	1,4-Xylene	2.34						
455	n-octane	22.74	19.44		66.06	66.06	14.50	82.00
	2-Phenylpropane	7.55	(22.74)	-	(77.26)			
	2-Phenylbutane	4.30						
	o-Isopropyltoluene	12.64						
	Dimethylethylbenzene	16.07						
	2,8-Decadiyne	3.63						
	Other Aromatics	33.06						
480	3-Methylheptane	6.39	22.20	5.46	57.82	63.29	14.50	81.36
	Methylbenzene	15.58	(25.97)	(6.39)	(67.64)			
	n-octane	25.97						

	Ethylbenzol	6.37						
	1,4-Dimethylbenzene	19.98						
	o-Ethyltoluene	8.41						
	1,2,3-Trimethylbenzene	10.90						
	2-Phenylpropane	1.78						
	m-Propyltoluene	1.65						
	Dimethylethylbenzene	1.69						
	Cyclopentacycloheptene	1.27						
505	Methylbenzene	7.56	59.03		26.47	26.47	14.50	64.61
	n-octane	69.04	(69.04)	-	(30.96)			
	Ethylbenzol	2.56						
	1,4-Dimethylbenzene	10.93						
	o-Ethyltoluene	4.33						
	1,2,3-Trimethylbenzene	5.58						
530	2-Methylheptane	1.13	3.13	6.01	76.36	82.37	14.50	85.03
	3-Methylheptane	1.17	(3.66)	(7.03)	(89.31)			
	n-octane	3.66						
	2,5-Dimethylheptane	4.73						
	Phenylethane	14.15						
	1,4-Dimethylbenzene	5.73						
	Propylbenzene	5.60						
	o-Ethyltoluene	16.60						
	1,2,3-Trimethylbenzene	22.42						
	2-Phenylbutane	6.98						
	o-Isopropyltoluene	7.83						
	Other Aromatics	10.01						

The selectivity of each of the catalysts for: isoparaffins, and aromatics are given in Tables A-3 (i & ii).

$$Selectivity = \frac{wt\,\%\,of\ \ either\ \ isoparaffins\ or\ aromatics\ \ formed}{wt\,\%\,of\ \ overall\ \ products\ \ formed}$$

Table A-3 (i): Selectivity of the Support and Zn/Alumina Catalysts for iso-paraffins, and aromatics

Rxn Temp (°C)	Composition of the products inclusive of volatile gases							
	Percentage assigned to component							
	Total Paraffins (n-octane), (%)	**Total Iso-paraffins (%)**	**Total Aromatics (%)**	**TOTAL Reformate Product=R**	**Dry volatile gases = X**	**Yield of reformate (%)**	**Selectivity for isoparaffins (%)**	**Selectivity for Aromatics (%)**
The n-octane feed								
	100	-	-	0	0	-	-	-
Reactor packed with Gamma-Alumina								
430	85.5	-	-	0	14.50	0	0	0
455	66.42 (77.69)	1.14 (1.33)	17.95 (20.99)	19.09	14.50	56.83	3.40	53.43
480	60.44 (70.69)	-	25.06 (29.31)	25.06	14.50	63.34	0	63.20
505	12.11 (14.16)	30.86 (36.09)	42.53 (49.74)	73.39	14.50	83.50	35.11	48.39
530	35.88 (41.97)	29.94 (35.02)	19.67 (23.0)	49.61	14.50	77.23	46.70	30.68
Reactor packed with Zn/Al_2O_3 Catalyst								
430	73.12 (85.52)	-	12.37 (14.47)	12.37	14.50	46.04	0	46.04
455	68.72 (80.37)	-	16.78 (19.63)	16.37	14.50	53.03	0	53.64
480	36.78	7.00	41.72	48.72	14.50	77.06	11.07	65.99

	(43.02)	(8.19)	(48.79)					
505	25.23 (29.51)	6.04 (7.07)	54.22 (63.42)	60.26	14.50	80.60	8.08	72.53
530	16.80 (19.65)	14.67 (17.16)	54.13 (63.19)	68.70	14.50	82.57	17.63	65.06

Table A-3 (ii): Selectivity of the Pt containing catalysts for iso-paraffins, and aromatics

Reactor packed with 0.50% Pt-Zn/Al_2O_3 catalyst								
430	78.34 (91.63)	-	7.16 (8.37)	7.16	14.50	33.06	0	33.06
455	39.95 (46.73)	4.57 (5.34)	40.98 (47.93)	45.55	14.50	75.85	7.61	68.24
480	14.49 (16.95)	8.19 (9.58)	62.81 (73.47)	71.01	14.50	83.05	9.58	73.45
505	61.40		24.10	24.10	14.50	62.44	0	62.43

	(71.81)	-	(28.19)					
530	11.35 (13.28)	11.68 (13.66)	62.47 (73.06)	74.15	14.50	83.64	13.18	70.47
	Reactor packed with 1.0% Pt-Zn/Al_2O_3 catalyst							
430	69.00 (80.70)	-	16.50 (19.30)	16.50	14.50	53.23	0	53.22
455	33.21 (38.84)	5.46 (6.39)	46.83 (54.77)	52.29	14.50	78.29	8.17	70.12
480	8.05 (9.42)	10.24 (11.98)	67.20 (78.60)	77.44	14.50	84.23	11.13	73.09
505	62.22 (72.77)	-	23.28 (27.23)	23.28	14.50	61.62	0	61.62
530	9.76 (11.42)	18.59 (21.74)	57.15 (66.84)	75.74	14.50	83.93	20.60	63.33
Reactor packed with 1.5% Pt-Zn/Al_2O_3 catalyst								
430	70.55 (82.52)	-	14.95 (17.48)	14.95	14.50	50.75	0	50.75
455	20.22 (23.65)	0.59 (0.69)	64.69 (75.66)	65.28	14.50	81.83	0.74	81.09
480	9.00 (10.53)	5.15 (6.02)	71.35 (83.45)	76.50	14.50	84.06	5.66	78.41
505	48.50 (56.73)	5.22 (6.10)	31.78 (37.17)	37.00	14.50	71.85	10.14	61.71
530	15.60 (18.25)	13.51 (15.80)	56.39 (65.95)	69.90	14.50	82.82	16.01	66.82
Reactor packed with 2.0% Pt-Zn/Al_2O_3 catalyst								
430	80.60 (94.27)	-	4.90 (5.73)	4.90	14.50	25.26	0	25.26
455	19.44		66.06	66.06	14.50	82.00	0	82.0

	(22.74)	-	(77.26)					
480	22.20 (25.97)	5.46 (6.39)	57.83 (67.64)	63.29	14.50	81.36	7.02	74.34
505	59.03 (69.04)	-	26.47 (30.96)	26.47	14.50	64.61	0	64.61
530	3.13 (3.66)	6.01 (7.03)	76.36 (89.31)	82.37	14.50	85.03	6.20	78.83

Table A-4: Typical product yields in a CCRU operation

Products	**Wt%**	**Average Wt%**	**Details**
H_2 Rich gas	6.5-8.0	7.25	$X = 7.25+7.25=14.5\%$ (X = Dry volatile gases: C_1, C_2, C_3, C_4)
LPG	2.5-12	7.25	
Reformate	80-91	85.50	R = Reformate f = Converted feed, N = Unconverted feed
			Let F be the n-octane fed to the reactor Let f be the n-octane consumed. $F = f + N = R + X + N$ $f = R+X$

The first two columns in the above table were extracted from the work of Kalra (2009), while the other columns are deductions made therein.

From Table A-4, *R*, *X*, *N* are the products of reforming. Thus, the yield of the desired product *R* can be quantified as

$$Yield = \frac{R}{f} = \left(\frac{R}{R+X}\right) \times 100\%$$

Where $X = 14.50$

APPENDIX B

GC-MS ANALYSIS RESULTS FOR THE FEED (n-octane)

NARICT, ZARIA

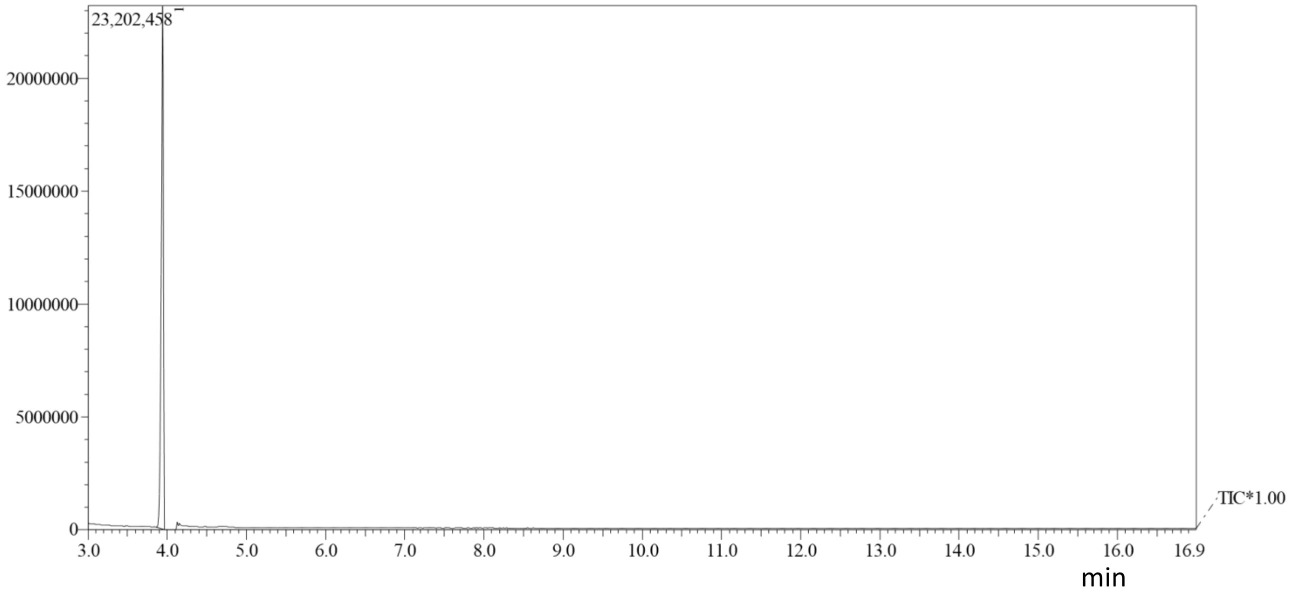
GCMS-QP2010 PLUS SHIMADZU, JAPAN

OLOWORISHE F. JOHN (SAMPLE-36)

Chromatogram

Chromatogram FEMI Sample

C:\GCMSsolution\OLOWORISHE F JOHN\FEMI015.qgd intensity



Method

[Comment]

===== Analytical Line 1 =====

[AOC-20i]
# of Rinses with Presolvent :4
# of Rinses with Solvent(post) :4
# of Rinses with Sample :3
Plunger Speed(Suction) : High
Viscosity Comp. Time :0.2 sec

Plunger Speed(Injection) : High
Syringe Insertion Speed : High
Injection Mode : Normal
Pumping Times :5
Inj. Port Dwell Time :0.3 sec
Terminal Air Gap : No
Plunger Washing Speed : High
Washing Volume :8 uL
Syringe Suction Position :0.0 mm
Syringe Injection Position :0.0 mm
Use 3 Solvent Vial :1 vial

[GC-2010]
Column Oven Temp. :60.0 °C
Injection Temp. :250.00 °C
Injection Mode : Split
Flow Control Mode : Linear Velocity
Pressure :100.2 kPa
Total Flow :6.2 mL/min
Column Flow :1.61 mL/min
Linear Velocity :46.3 cm/sec
Purge Flow :3.0 mL/min
Split Ratio :1.0
High Pressure Injection : OFF
Carrier Gas Saver : OFF
Splitter Hold : OFF
Oven Temp. Program

Rate	Temperature(°C)	Hold Time(min)
-	60.0	4.00
8.00	160.0	2.00

< Ready Check Heat Unit >

Column Oven : Yes

SPL2 : Yes

MS : Yes

< Ready Check Detector(FTD) >

< Ready Check Baseline Drift >

< Ready Check Injection Flow >

SPL2 Carrier : Yes

SPL2 Purge : Yes

< Ready Check APC Flow >

< Ready Check Detector APC Flow >

External Wait : No

Equilibrium Time :3.0 min

[GC Program]

[GCMS-QP2010 Plus]

IonSourceTemp
:200.00 °C
Interface Temp.
:250.00 °C
Solvent Cut Time
:2.50 min
Detector Gain Mode :
Relative
Detector Gain :0.00 kV
Threshold :3000

[MS Table]
--Group 1 - Event 1--
Start Time :3.00 min
End Time :17.00 min
ACQ Mode : Scan
Event Time :0.50 sec
Scan Speed : 555
Start m/z :40.00
End m/z :300.00

Sample Inlet Unit :
GC

[MS Program]
Use MS Program : Peak Report
OFF TIC

Peak# R.Time F.Time Area Area% Height Height% A/H Mark
I.Time Name
1 3.943 3.858 3.967 100.00 100.00 1.96
4551958423171953
45519584 100.00 23171953 100.00

Spectrum

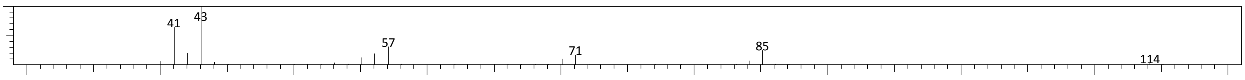
Line#:1 R.Time:3.9(Scan#:114)

MassPeaks:34

RawMode:Single 3.9(114) BasePeak:43(7069837)

BG Mode:4.0(118) Group 1 - Event 1

100



30 40 50 60 70 80 90 100 110

m/z

Spectrum Comparison

Library

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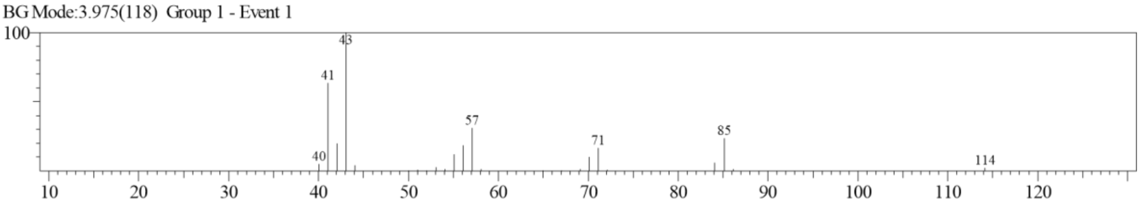
<< Target >>

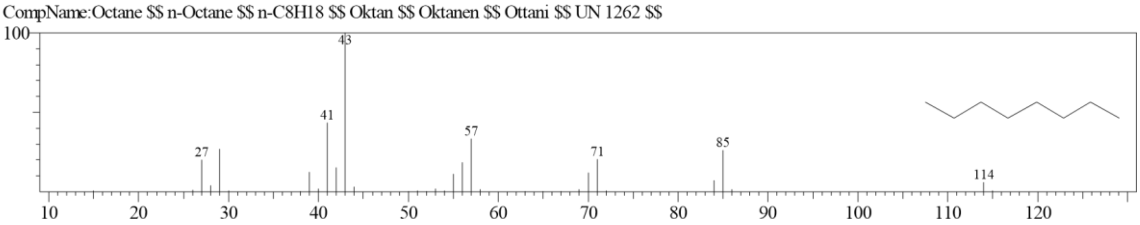
Line#:1 R.Time:3.942(Scan#:114) MassPeaks:34

RawMode:Single 3.942(114) BasePeak:43.05(7069837)



Hit#:1 Entry:4163 Library:NIST05.LIB

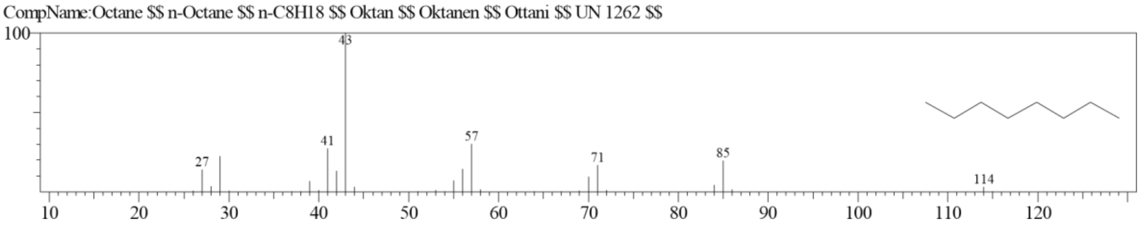
SI:96 Formula:C8H18 CAS:111-65-9 MolWeight:114 RetIndex:816



CompName:Octane $$ n-Octane $$ n-C8H18 $$ Oktan $$ Oktanen $$ Ottani $$ UN 1262 $$

Hit#:2 Entry:3265 Library:NIST05s.LIB

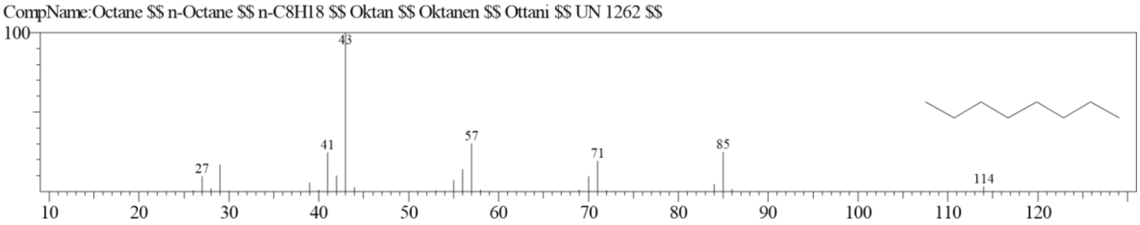
SI:94 Formula:C8H18 CAS:111-65-9 MolWeight:114 RetIndex:816



CompName:Octane $$ n-Octane $$ n-C8H18 $$ Oktan $$ Oktanen $$ Ottani $$ UN 1262 $$

Hit#:3 Entry:3268 Library:NIST05s.LIB

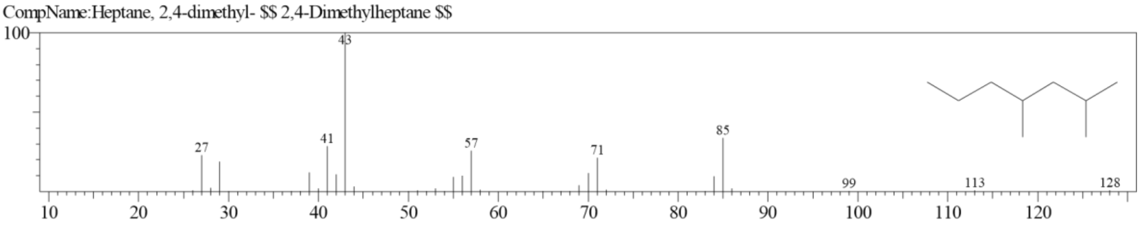
SI:93 Formula:C8H18 CAS:111-65-9 MolWeight:114 RetIndex:816



CompName:Octane $$ n-Octane $$ n-C8H18 $$ Oktan $$ Oktanen $$ Ottani $$ UN 1262 $$

Hit#:4 Entry:5018 Library:NIST05s.LIB

SI:92 Formula:C9H20 CAS:2213-23-2 MolWeight:128 RetIndex:788

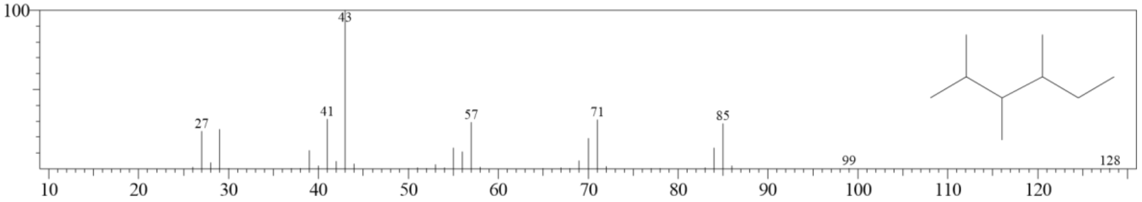


CompName:Heptane, 2,4-dimethyl- $$ 2,4-Dimethylheptane $$

Hit#:5 Entry:7261 Library:NIST05.LIB

SI:91 Formula:C9H20 CAS:921-47-1 MolWeight:128 RetIndex:724

CompName:Hexane, 2,3,4-trimethyl- $$ 2,3,4-Trimethylhexane $$



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