

**THE CRACKING OF GASOIL TO PRODUCE BENZENE, TOLUENE  
AND XYLENE (BTX)**

**BY**

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**2006/24237EH**

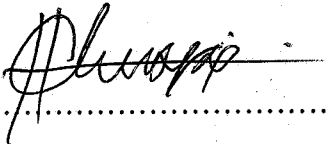
**SUBMITTED TO**

**THE DEPARTMENT OF CHEMICAL ENGINEERING  
FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA  
NIGERIA**

**NOVEMBER 2011**

## DECLARATION

I do hereby declare that this research work 'CRACKING OF GAS OIL TO PRODUCE BTX', was conducted by me, CHIJOKE NDUBUEZE OKOLI, under the diligent supervision of Dr M. O. Edoga. I have neither copied someone's work nor has someone else done mine for me. All literature cited have been duly acknowledged in the reference.



OKOLI NDUBUEZE CHIJOKE

02/12/2011

Date

## DEDICATION

This work is dedicated to the Almighty God. And also to my very wonderful parents and siblings, for their love and support all through the course of my study.

## ACKNOWLEDGEMENT

I am grateful to God Almighty for seeing me through my studies and for His abundant love and favor in my life, Baba God you too much. My sincere appreciation goes to my dear parents for the unadulterated love and full support they have given me over the years, God bless you greatly.

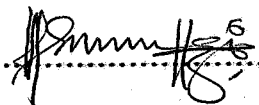
I am not unaware of the hands and pockets that have in one way or the other brought about the success of this research work. I wish to thank most especially my uncle, Mr. Forster Okoli, my aunt, Mrs. Uzor Ezeani and my other numerous uncles, aunts, cousins and nephews for their love and financial support towards my academic pursuits.

My friends; Uche Uchendu Igbokwe, Daniel Aliu, Chimezie Uwandu, Emeka Ezenwa, Hillary Mbaogu, Chukwuma Ugbah, Ega Owoicho, Olaibi Aminat, Adeola Afolayan, Ayodele Kadiri, Nimya Dashe, Jenifer Nnaji, Oluwadare Akinbode, and numerous others. You guys are the best a man could ever ask for in friends. And also to my fellow chemical engineering classmates, it was an honour knowing you all and may we all proudly keep the chemical engineering flag flying high.

Finally, I wish to express my profound gratitude to my project supervisor, Dr. M. O. Edoga whose useful instructions, fatherly concern and motivational support have over the months and years culminated in making this project work a huge success. May God bless you greatly Sir. And to all members of staff of the chemical engineering department, thank you all very much for the time, effort and resources you unselfishly bestowed upon me. God bless you all.

## CERTIFICATION

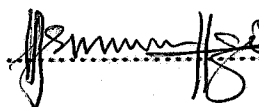
This is to certify that this research work titled 'Cracking of Gas Oil to Produce BTX' was carried out by me, Okoli Ndubueze Chijioke with matriculation number 2006/24237EH under the supervision of Dr. M. O. Edoga and submitted to the Chemical Engineering Department, Federal University of Technology, Minna, as part of the requirement for the award of Bachelor of Engineering (B. Eng.) Degree in Chemical Engineering.

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## ABSTRACT

The refining industry has over the decades, brought about great advancement in terms of economic and societal growth as well as technologically. Cracking is just one of the many processes that were invented over time in the refining industry. The cracking of gasoil to produce BTX, being the topic of this project work was carried out with the aim of performing the cracking procedure. The procedure chosen for the experiment involved the fluid catalytic cracking of the Gasoil to produce Naphtha, the production of Hydrogen gas, and then the catalytic reforming of the Naphtha formed to obtain the reformat from which the BTX components are obtained. In the laboratory, the Hydrogen gas was successfully produced. But while in the process of reforming the Naphtha, there was a huge explosion. This explosion led to the complete destruction of equipments and materials for the experiment, thereby leading to the inability to see the experiment to completion. In conclusion, Hydrogen production for the hydrogenation of Naphtha was successful, but the BTX production was not. Investigations into the cause of the explosion revealed that the material used for the reactor fabrication (Aluminium), as well as the explosive nature of the Hydrogen and Naphtha mixture being heated inside the reactor were to blame. Recommendations were therefore made for further studies into this topic and also for an alternative material for the reactor vessel (Stainless Steel).

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## CHAPTER ONE

### 1.0 INTRODUCTION

The main feedstock for the refining industry is crude oil or petroleum (James, 2001). In its raw, unprocessed state, this crude is of little value or importance to us as humans (economically, industrially and otherwise). It is this singular but consequential limitation that therefore drives the need to find ways of improving upon this raw crude in such a manner that its great potential is realized. Over the decades, very many techniques of converting crude oil into more valuable products have been researched, discovered and implemented. These crude oil reforming processes are quite numerous and find use in various stages of the refining process. Some of these include; coking, distillation, fractionation and cracking, etc.

Cracking, as may be implied from the name, is the process by which large hydrocarbon molecules are converted into smaller ones. It is also known as destructive distillation or pyrolysis. Here, complex organic molecules or heavy hydrocarbons are broken down into simpler molecules, by the break-down of carbon-carbon bonds in the structure of the heavy parent material. Simply put, cracking is the process of breaking long-chain hydrocarbons into short ones. The process of Cracking is carried out either at high temperatures (thermal cracking), or with the aid of a catalyst and high pressure (catalytic cracking and hydro-cracking). The rate of cracking and the end products are therefore strongly dependent on the temperature and/or the presence of catalysts (David et al., 2006). The applications of cracking in refining processes are numerous and indispensable. Oil refinery cracking processes allow for the production of "light" products such as liquefied petroleum gas (LPG) and gasoline from heavier crude oil distillation fractions such as gasoil-which is a make-up of very large hydrocarbon molecules (Speight, 1999).

Gasoil is a liquid petroleum product with a boiling range temperature of 200-370 °C and an ignition temperature of over 55 °C that is typically used as a fuel for boilers, furnaces and internal combustion engines (Schleyer, 2001). It is a heavy by-product of heavier crude oil distillation fractions and can still be broken down into lighter products. Gasoil, because of its

very high temperature range and great chemical complexity, cannot be distilled into lighter fractions or distillates. For this to be overcome, other techniques for its breakdown must be sought. The cracking or forced breakdown process of the gas oil presents the best option. The cracking of gasoil usually yields a wide range of light weight organic products such as liquefied petroleum gas (LPG), jet fuels and BTX- which is a mixture of aromatic hydrocarbons, i.e. Benzene, Toluene and Xylene; etc (James, 2001) .

BTX (Benzene, Toluene and Xylene) is an aromatic mixture of hydrocarbons that is obtained as a product in certain refining processes. These compounds are known as aromatics, by reason of having at least one benzene ring and because of their physical property of having a sweet smell (Osei, 2000). They differ chemically from other organic compounds because of the ring formation of their structures. The mixture of these three compounds (BTX) in gasoil is obtained mainly by the cracking process. When the mixture is obtained, it can be further separated into individual components via other simpler means of separation.

The cracking of gasoil to produce BTX is till date an on-going research that has continued and will continue to yield surprising results by the day. BTX, because of the unique nature of the mixture, especially its toxic and poisonous nature, has become a grey area of debate in terms of production and handling (Schleyer, 2001). But the negative effects of these aromatic compounds on humans, though harmful, are almost over-shadowed by the fact that the uses of BTX are quite numerous and inexhaustible. Maximum protection against poisoning and bodily harm must therefore be fully observed during the cracking process, in order to avoid severe anatomical reactions and possibly death.

The cracking of gasoil to produce BTX is of great economic importance in the present era and holds a lot of unimaginable prospects for the future. Therefore, this research project could not have come at a better time.

## 1.1 Aims and Objectives

The aim of this research project is to:

- To perform the cracking of gasoil to produce BTX.

The objective of this research project is/are to:

- To perform the cracking process under appropriate conditions, so as to yield best results.
- To improve upon the process of cracking gasoil to produce BTX.

## 1.2 Approach

Cracking is a very extensive and expensive procedure to undertake. Also, the poisonous nature of the BTX mixture product can make the cracking process all the more grueling. It is therefore necessary that any technique chosen to be used for achieving this project be safe, efficient and relatively cheap. All experiments to be conducted for this research will therefore be done in the chemical engineering laboratory, FUT Minna, under proper supervision, except for where/when it becomes absolutely necessary to carry out an experiment outside the stipulated premises. The feed or gasoil will be obtained from the best sources (possibly from any refinery deemed appropriate, in keeping with cost and quality expectations). And the cracking process will be performed under the best of conditions, with appropriate equipments and with keeping to proper safety protocols, with minimum threat to human lives and wellbeing.

## 1.3 Justification

Any new knowledge achieved from this work will be useful in improving upon the efficiency of the cracking of gasoil to produce BTX economically, process-wise etc. While previous studies may have been done extensively on this research topic, this present work will try to fill in gaps left out by previous works. Also, the aromatics BTX are of great financial value because of their use in numerous pharmaceutical, petrochemical, chemical and manufacturing industries. This research work will therefore open frontiers into how these aromatics can be used in other to minimize cost while also maximizing profit in these industries.

## CHAPTER TWO

### 2.0 LITERATURE REVIEW

#### 2.1 Cracking

The process of breaking higher hydrocarbons with high boiling points into a variety of lower hydrocarbons that are more volatile and have lower boiling points is called cracking. It is defined as the conversion of large hydrocarbon molecules into smaller ones or the process of breaking long-chain hydrocarbons into shorter ones (Matar and Hatch, 2001).

More loosely, outside the field of petroleum chemistry, the term cracking is used to describe any type of splitting of molecules under the influence of heat, catalysts and solvents, such as in processes of destructive distillation or pyrolysis (Reza, 2000).

##### 2.1.1 Invention and History of Cracking

Cracking was invented in 1855 by Silliman. Its discovery came at a time when the further breakdown of crude oil distillates was highly sought. There was also a need at the time, for an improvement in the refining process for fuels that would prevent engine knocking and increase engine efficiency. Especially for the new high compression automobile engines that were being designed. The processes that were invented to improve the yield of gasoline from crude oil were known as cracking (Lappas, 1997).

More specifically, the thermal cracking method (also known as "Shukhov cracking process") was invented by Russian engineer Vladimir Shukhov and patented in 1891 in the Russian empire, patent no. 12926, November 27, 1891. This process was modified by the American engineer William Merriam Burton and patented as U.S. patent 1,049,667 on June 8, 1908.

The history of cracking is as follows:

1855 - The cracking of petroleum was discovered by Silliman in 1855, but it did not become a matter of practical interest to oil refiners until later on.

1913 - In 1913, a US patent for the thermal cracking of crude oil was issued to William Merriam Burton (No.1049667). A crude petroleum mixture of various hydrocarbons can be separated into several groups of constituents by physical means, commonly distillation.

1926 - Kellogg set up one of the first petroleum laboratories in 1926 to commercialize and then license the technology. This led to the building of some 130 units in the US and abroad.

1927 - In April 1927 he (Kellogg) discovered a chemical catalysis process to "crack" petroleum and yield high-octane gasoline, a development that, had it been available three years earlier, might have derailed GM's efforts to add tetraethyl lead to gasoline.

1936 - Thermal cracking was the principal source of gasoline production until Eugene Houdry first introduced commercial catalytic cracking in 1936.

2005 - The first batch of petroleum polymer resin is scheduled for production in June 2005. There is a history behind this development. An original process to produce hydrocarbon resin from still products of the cracking process was developed in Russia at the end of the 20th century (Clause et al., 1998).

### **2.1.2 Types and Techniques of Cracking**

Cracking processes break down heavier hydrocarbon molecules (high boiling point oils) into lighter products such as petrol and diesel. These processes include catalytic cracking, thermal cracking and Hydrocracking, and other sub-cracking techniques, e.g. fluid catalytic cracking, steam cracking, etc.

#### **2.1.2.1 Catalytic cracking**

This is used to convert heavy hydrocarbon fractions obtained by vacuum distillation into a mixture of more useful products such as petrol and light fuel oil. In this process, the feedstock undergoes a chemical breakdown, under controlled heat (450 – 500 °C) and pressure, in the presence of a catalyst - a substance which promotes the reaction without itself being chemically changed. The catalyst is usually a mixture of aluminium oxide and silica. Most recently, the

introduction of synthetic zeolite catalysts has allowed much shorter reaction times and improved yields and octane numbers of the cracked gasoline.

Small pellets of silica - alumina or silica - magnesia have proved to be the most effective catalysts. The cracking reaction yields petrol, LPG, unsaturated olefin compounds, cracked gas oils, a liquid residue called cycle oil, light gases and a solid coke residue. Cycle oil is recycled to cause further breakdown and the coke, which forms a layer on the catalyst, and is removed by burning. The other products are passed through a fractionator to be separated and separately processed. Higher hydrocarbons can also be cracked at lower temperature (600 - 650 K) and lower pressure (2 atmospheres) in the presence of a suitable catalyst. Catalytic cracking produces gasoline of higher octane number and therefore this method is used for obtaining better quality gasoline. A typical catalyst used for this purpose is a mixture of silica, alumina and manganese-dioxide. In newer designs, cracking takes place using a very active zeolite-based catalyst in a short-contact time vertical or upward sloped pipe called the "riser". Pre-heated feed is sprayed into the base of the riser via feed nozzles where it contacts extremely hot fluidized catalyst at 1230 °F to 1400 °F (665 °C to 760 °C). The hot catalyst vaporizes the feed and catalyzes the cracking reactions that break down the high molecular weight oil into lighter components including LPG, gasoline, and diesel. The catalyst-hydrocarbon mixture flows upward through the riser for just a few seconds and then the mixture is separated via cyclones. The catalyst-free hydrocarbons are routed to a main fractionator for separation into fuel gas, LPG, gasoline, naphtha, light cycle oils used in diesel and jet fuel, and heavy fuel oil (James, 2001).

#### **2.1.2.2 Thermal cracking**

This process is the oldest technology in cracking. The process occurs via the Breaking down of large molecules by heating at high temperature and pressure is termed as thermal cracking. Thermal cracking is further classified into the following classes.

**Liquid phase thermal cracking process:** The higher boiling fractions e.g., fuel oil, lubricating oil are converted into low boiling fractions by heating the liquids at a temperature of 750 K, under a pressure of about 10 atmospheres.



Vapour phase thermal cracking process: Low boiling fraction e.g., kerosene is cracked in the vapour phase at a temperature of about 875 K and under a pressure of 3 atmospheres.

Heat is used in this process to break down the residue from vacuum distillation. The lighter elements produced from this process can be made into distillate fuels and petrol. Cracked gases are converted to petrol blending components by alkylation or polymerization. Naphtha is upgraded to high quality petrol by reforming. Gas oil can be used as diesel fuel or can be converted to petrol by Hydrocracking. The heavy residue is converted into residual oil or coke which is used in the manufacture of electrodes, graphite and carbide (James, 2001).

### **2.1.2.3 Fluid catalytic cracking**

Is a form of catalytic cracking that uses a catalyst in the form of a very fine powder which flows like a liquid when agitated by steam, air or vapour. Feedstock entering the process immediately meets a stream of very hot catalyst and vaporizes. The resulting vapours keep the catalyst fluidized as it passes into the reactor, where the cracking takes place and where it is fluidized by the hydrocarbon vapour. The catalyst next passes to a steam stripping section where most of the volatile hydrocarbons are removed. It then passes to a regenerator vessel where it is fluidized by a mixture of air and the products of combustion which are produced as the coke on the catalyst is burnt off. The catalyst then flows back to the reactor. The catalyst thus undergoes a continuous circulation between the reactor, stripper and regenerator sections (Reza, 2000).

The FCC is the most important conversion process used in petroleum refineries. It is widely used to convert the high-boiling, high-molecular weight hydrocarbon fractions of petroleum crude oils to more valuable gasoline, olefinic gases and other products. Cracking of petroleum hydrocarbons was originally done by thermal cracking which has been almost completely replaced by catalytic cracking because it produces more gasoline with a higher octane rating. It also produces by-product gases that are more olefinic, and hence more valuable, than those produced by thermal cracking (Reza, 2000).

The feedstock to an FCC is usually that portion of the crude oil that has an initial boiling point of 340 °C or higher at atmospheric pressure and an average molecular weight ranging from about

200 to 600 or higher. This portion of crude oil is often referred to as heavy gas oil. The FCC process vaporizes and breaks the long-chain molecules of the high-boiling hydrocarbon liquids into much shorter molecules by contacting the feedstock, at high temperature and moderate pressure, with a fluidized powdered catalyst (Speight, 1999).

### **2.1.3 Chemistry of the Cracking Processes**

"Cracking" breaks larger molecules into smaller ones, through thermic or catalytic method. The reactions that take place during this rupture are shown below.

#### **2.1.3.1 Chemistry of thermal cracking process**

The thermal cracking process follows a homolytic mechanism, that is, bonds break symmetrically and thus pairs of free radicals are formed. William Merriam Burton developed one of the earliest thermal cracking processes in 1912 which operated at 700 - 750 °F (370 - 400 °C) and an absolute pressure of 90 psi (620 kPa) and was known as the Burton process. Shortly thereafter, in 1921, C.P. Dubbs, an employee of the Universal Oil Products Company, developed a somewhat more advanced thermal cracking process which operated at 750°F - 860 °F (400°C - 460 °C) and was known as the Dubbs process. The Dubbs process was used extensively by many refineries until the early 1940s when catalytic cracking came into use (Speight, 1999).

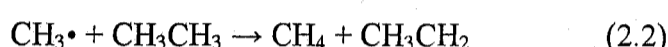
Modern high-pressure thermal cracking operates at absolute pressures of about 7,000 kPa. An overall process of disproportionation can be observed, where "light", hydrogen-rich products are formed at the expense of heavier molecules which condense and are depleted of hydrogen. The actual reaction is known as homolytic fission and produces alkenes, which are the basis for the economically important production of polymers.

A large number of chemical reactions take place during steam cracking, most of them based on free radicals. Computer simulations aimed at modeling what takes place during steam cracking have included hundreds or even thousands of reactions in their models. The main reactions that take place include:

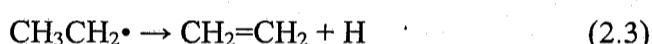
**Initiation;** includes reactions where a single molecule breaks apart into two free radicals. Only a small fraction of the feed molecules actually undergo initiation, but these reactions are necessary to produce the free radicals that drive the rest of the reactions. In steam cracking, initiation usually involves breaking a chemical bond between two carbon atoms, rather than the bond between a carbon and a hydrogen atom.



**Hydrogen abstraction;** occurs where a free radical removes a hydrogen atom from another molecule, turning the second molecule into a free radical.



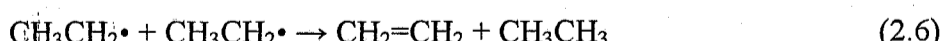
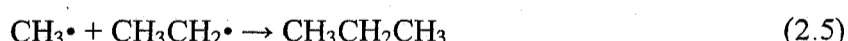
**Radical decomposition;** occurs where a free radical breaks apart into two molecules, one an alkene, the other a free radical. This is the process that results in the alkene products of steam cracking.



**Radical addition;** the reverse of radical decomposition, occurs where a radical reacts with an alkene to form a single, larger free radical. These processes are involved in forming the aromatic products that result when heavier feedstock are used.



**Termination reactions;** occur when two free radicals react with each other to produce products that are not free radicals. Two common forms of termination are *recombination*, where the two radicals combine to form one larger molecule, and *disproportionation*, where one radical transfers a hydrogen atom to the other, giving an alkene and an alkane (Speight, 1999).



#### 2.1.4.2 Chemistry of catalytic cracking process

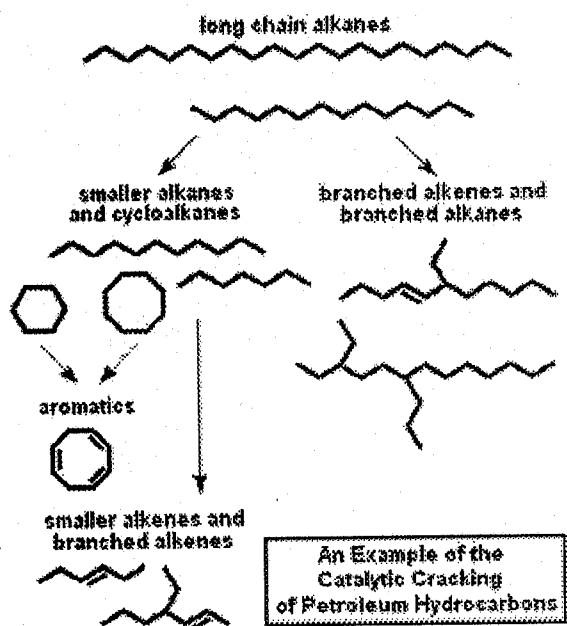
The catalytic cracking process involves the presence of acid catalyst (usually solid acids such as silica-alumina and zeolites) which promote a heterolytic (asymmetric) breakage of bonds yielding pairs of ions of opposite charges, usually a carbocation and the very unstable hydride anion. Carbon-localized free radicals and cations are both highly unstable and undergo processes of chain rearrangement, C-C scission in position beta as in cracking, and intra- and intermolecular hydrogen transfer or hydride transfer. In both types of processes, the corresponding reactive intermediates (radicals, ions) are permanently regenerated, and thus they proceed by a self-propagating chain mechanism. The chain of reactions is eventually terminated by radical or ion recombination (James, 2001).

#### 2.1.3.3 Chemistry of fluid catalytic cracking process

In plain language, the fluid catalytic cracking process breaks large hydrocarbon molecules into smaller molecules by contacting them with powdered catalyst at a high temperature and moderate pressure which first vaporizes the hydrocarbons and then breaks them. The cracking reactions occur in the vapour phase and start immediately when the feedstock is vaporized in the catalyst riser.

Figure 2.1 below is a very simplified schematic diagram that exemplifies how the process breaks high boiling, straight-chain alkane (paraffin) hydrocarbons into smaller straight-chain alkanes as well as branched-chain alkanes, branched alkenes (olefins) and cycloalkanes (naphthenes). The breaking of the large hydrocarbon molecules into smaller molecules is more technically referred to by organic chemists as *scission* of the carbon-to-carbon bonds.

As depicted in Figure 2, some of the smaller alkanes are then broken and converted into even smaller alkenes and branched alkenes such as the gases ethylene, propylene, butylenes, and isobutylenes. Those olefinic gases are valuable for use as petrochemical feedstock. The propylene, butylene and isobutylene are also valuable feedstock for certain petroleum refining processes that convert them into high-octane gasoline blending components.



**Figure 2.1 Schematic example for FCC process**

As also depicted in Figure 2.1, the cycloalkanes (naphthenes) formed by the initial breakup of the large molecules are further converted to aromatics such as benzene, toluenes and xylenes which boil in the gasoline boiling range and have much higher octane ratings than alkanes. (Reza Sadeghbeigi, 2000)

#### **Catalysts for FCC;**

Modern FCC catalysts are fine powders with a bulk density of 0.80 to 0.96 g/cc and having a **particle size distribution** ranging from 10 to 150  $\mu\text{m}$  and an average particle size of 60 to 100  $\mu\text{m}$ . **The design and operation** of an FCC unit is largely dependent upon the chemical and physical **properties of the catalyst**. The desirable properties of an FCC catalyst are:

- **Good stability to high temperature and to steam**
- **High activity**
- **Large pore sizes**
- **Good resistance to attrition**
- **Low coke production**

Zeolite is the primary active component and can range from about 15 to 50 weight percent of the catalyst. The zeolite used in FCC catalysts is referred to as faujasite or as *Type Y* and is

silicon atom at the center and four oxygen atoms at the corners. It is a molecular sieve with a distinctive lattice structure that allows only a certain size range of hydrocarbon molecules to enter the lattice. In general, the zeolite does not allow molecules larger than 8 to 10 nm (i.e., 80 to 90 angstroms) to enter the lattice (Stepanov et al., 2001).

#### 2.1.4 Applications of Cracking

Oil refinery cracking processes allow for the production of "light" products such as liquefied petroleum gas (LPG) and gasoline from heavier crude oil distillation fractions such as gasoil and residues. Fluid catalytic cracking produces a high yield of gasoline and LPG, while Hydrocracking is a major source of jet fuel, diesel fuel, naphtha and LPG (Reza, 2000).

Thermal cracking is currently used to "upgrade" very heavy fractions, or to produce light fractions or distillates, burner fuel and/or petroleum coke. Two extremes of the thermal cracking in terms of product range are represented by the high-temperature process called "steam cracking" or pyrolysis ( 750 °C to 900 °C or more) which produces valuable ethylene and other feedstock for the petrochemical industry, and the milder-temperature delayed coking ( 500 °C) which can produce, under the right conditions, valuable needle coke, a highly crystalline petroleum coke used in the production of electrode and for the steel and aluminium industries (King, 1981).

### 2.2 Gasoil

Gasoil is a fraction obtained from petroleum distillation, either as a distillate or a residue. Broadly speaking, gasoil is any liquid petroleum product that is burned in a furnace or boiler for the generation of heat or used in an engine for the generation of power and oils burned in cotton or wool-wick burners. In this sense, diesel is a type of gasoil. Gasoil is made of long hydrocarbon chains, particularly alkanes, cycloalkanes and aromatics (Lappas, 1997). The term gasoil is also used in a stricter sense to refer only to the heaviest commercial fuel that can be obtained from crude oil, heavier than gasoline and naphtha. An oily liquid obtained in the fractional distillation of petroleum, boiling between the kerosene and lubricating oil fractions: used especially as a diesel fuel and heating oil. Gasoil is a liquid petroleum product with a

boiling range temperature of 200-370 °C and an ignition temperature over 55 °C that is typically used as a fuel for boilers, furnaces and internal combustion engines. It is a heavy by-product of heavier crude oil distillation fractions and can still be separated into lighter products (Edgar, 1983).

### 2.2.1 Classification of Gasoil

There are six grades of gasoil, numbered 1 through 6. This classification system was originally based on early refining and combustion engineering practices and nomenclature. Some specifications have changed over the years to reflect new refining practices and refinery by-products. Other organizations have published modified versions of the original six fuel specifications to assist operators of older equipment find appropriate fuels from current refinery products. The boiling point and carbon chain length of the fuel increases with fuel oil number. Viscosity also increases with number, and the heaviest oil has to be heated to get it to flow. Price usually decreases as the fuel number increases.

- **Number 1 gasoil** is volatile distillate oil intended for vaporizing pot-type burners. It is the kerosene refinery cut that boils off right after the heavy gasoil cut used for gasoline. Older names include coal oil, stove oil and range oil.
- **Number 2 gasoil** is a distillate home heating oil. Trucks and some cars use similar diesel fuel with a certain number limit describing the ignition quality of the fuel. Both are typically obtained from the light gasoil cut. Gasoil refers to the process of distillation. Crude oil is heated, becomes a gas and then condenses.
- **Number 3 gasoil** is a distillate oil for burners requiring low-viscosity fuel. ASTM merged this grade into the number 2 specification, and the term has been rarely used since the mid 20th century.
- **Number 4 gasoil** is a commercial heating oil for burner installations not equipped with preheaters. It may be obtained from the heavy gas oil cut.
- **Number 5 gasoil** is a residual-type industrial heating oil requiring preheating to between 170 and 220 degrees Fahrenheit for proper atomization at the burners. This fuel is

sometimes known as Bunker B. It may be obtained from the heavy gas oil cut, or it may be a blend of residual oil with enough number 2 oil to adjust viscosity until it can be pumped without preheating.

- **Number 6 gasoil** is a high-viscosity residual oil requiring preheating to between 220 to 260 degrees Fahrenheit. Residual means the material remaining after the more valuable cuts of crude oil have boiled off. The residue may contain various undesirable impurities including 2 percent water and one-half percent mineral soil. This fuel may be known as residual fuel oil (RFO), by the Navy specification of Bunker C, or by the Pacific Specification of PS-400 (Clause, 1998).

### 2.2.2 Uses of Gasoil

Gasoil has two basic uses—as the primary component in the production of gasoline and fuels and as a feedstock for the production of olefin and aromatic petrochemical products. Gas oil is used as a chemical feedstock for steam cracking, although it is generally preferred less than naphtha and natural gas liquids [LPG], as its use depends primarily on feedstock and ethylene co-product pricing structures. Gas oil is predominantly used in the fuel markets. In the United States gas oil is consumed in refining processes to produce gasoline blending components. In Western Europe and Asia, little upgrading of gas oil is done (compared with the United States) (Lovink et al., 1995).

Gasoil has many uses; it heats homes and businesses and fuels trucks, ships and some cars. A small amount of electricity is produced by diesel, but it is more polluting and more expensive than natural gas. It is often used as a backup fuel for peaking power plants in case the supply of natural gas is interrupted or as the main fuel for small electrical generators. In Europe, the use of diesel is generally restricted to cars (about 40 %), SUVs (about 90 %), and trucks and buses (virtually all). The market for home heating using gasoil, called heating oil, has decreased due to the widespread penetration of natural gas. However, it is very common in some areas. Heavy gasoil continue to be used in the boiler "lighting up" facility in many coal-fired power plants (Lovink et al., 1995).



**CRACKING OF GAS OIL TO PRODUCE BENZENE, TOLUENE AND  
XYLENE (BTX)**

**BY**

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## 2.3 Aromaticity

Aromatic hydrocarbons, so named for their characteristic strong sweet odour, are found in Nature in volcanoes and wood fires. They are also produced commercially and have many Industrial uses. Most notably as a solvent for numerous materials and as a fuel additive. Benzene, toluene and xylene, the most widely used aromatic hydrocarbons, are very useful chemicals and are discussed here (Schleyer and Paul, 2001).

### 2.3.1 History

The first known use of the word "aromatic" as a *chemical* term—namely, to apply to compounds that contain the phenyl radical—occurs in an article by August Wilhelm in 1855. If this is indeed the earliest introduction of the term, it is curious that Hofmann says nothing about why he introduced an adjective indicating olfactory character to apply to a group of chemical substances, only some of which have notable aromas. It is the case, however, that many of the most odoriferous organic substances known are terpenes, which are not aromatic in the chemical sense. But terpenes and benzenoid substances do have a chemical characteristic in common, namely higher unsaturation indices than many aliphatic compounds, and Hofmann may not have been making a distinction between the two categories. The cyclohexatriene structure for benzene was first proposed by August Kekule in 1865. Over the next few decades, most chemists readily accepted this structure, since it accounted for most of the known isomeric relationships of aromatic chemistry. However, it was always puzzling that this purportedly highly-unsaturated molecule was so unreactive toward addition reactions (David, 2005).

### 2.3.2 Chemistry of Aromatics

Aromaticity is a chemical property in which a conjugated ring of unsaturated bonds, lone pairs, or empty orbitals exhibit stabilization stronger than would be expected by the stabilization of conjugation alone. It can also be considered a manifestation of cyclic delocalization and of resonance. This is usually considered to be because electrons are free to cycle around circular arrangements of atoms which are alternately single- and double-bonded to one another. These bonds may be seen as a hybrid of a single bond and a double bond, each bond in the ring

identical to every other. This commonly-seen model of aromatic rings, namely the idea that benzene was formed from a six-membered carbon ring with alternating single and double bonds (cyclohexatriene), was developed by Kekulé. The model for benzene consists of two resonance forms, which corresponds to the double and single bonds superimposing to give rise to six one-and-a-half bonds (Schleyer, 2001).

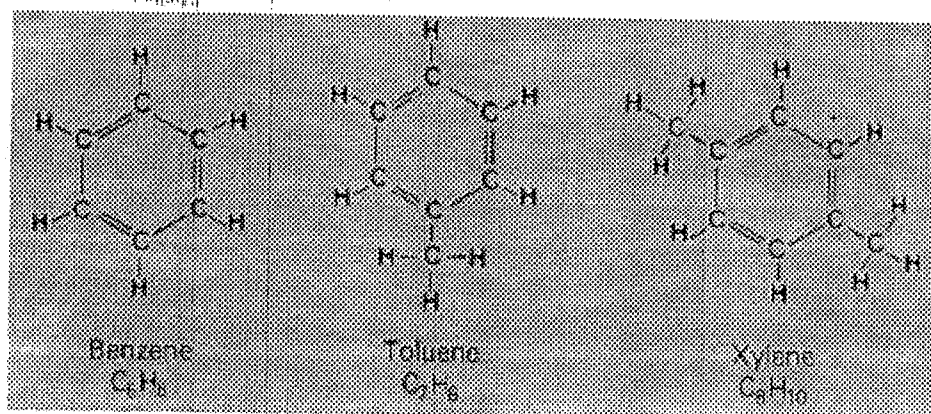


Figure 2.2: Structure of Benzene, Toluene and Xylene

### 2.3.3 Characteristics of Aromatic Compounds

Some physical and chemical properties of the aromatic compounds are shown below.

Table 2.1: Physical Characteristics of Some Commonly Known Aromatics

Compound	Mole weight g mole <sup>-1</sup>	Density g ml <sup>-1</sup>	Boiling point °C	Water solubility mg l <sup>-1</sup>	Vapour pressure mmHg	Log K <sub>ow</sub>
Benzene	78	0.88	80.1	1780	76	2.13
Toluene	92	0.87	110.8	535	22	2.69
o-Xylene	106	0.88	144.4	175	5	2.77
m-Xylene	106	0.86	139	135	6	3.20
p-Xylene	106	0.86	138.4	198	6.5	3.15
Ethylbenzene	106	0.87	136.2	152	7	3.15

### 2.3.4 Importance of Aromatic Compounds

Aromatic compounds are important in industry. Key aromatic hydrocarbons of commercial interest are benzene, toluene and xylene. About 35 million tonnes are produced worldwide every year. They are extracted from complex mixtures obtained by the refining of oil or by distillation of coal tar, and are used to produce a range of important chemicals and polymers, including styrene, phenol, aniline, polyester and nylon.

Other aromatic compounds play key roles in the biochemistry of all living things. Four aromatic amino acids histamine, phenylalanine, tryptophan, and tyrosine, each serve as one of the 20 basic building blocks of proteins. Further, all 5 nucleotides (adenine, thymine, cytosine, guanine, and uracil) that make up the sequence of the genetic code in DNA and RNA are aromatic purines or pyrimidines. (Axens Process Brochures for Octanizing and Aromizing Processes. 2002)

### 2.4 BTX

This acronym stands for Benzene, Toluene and Xylene. BTX is a mixture of the aromatic compounds; Benzene, Toluene and Xylene that is obtained via several processes (natural and induced) and can be separated into their individual constituents if desired. Trace amounts of these aromatics (BTX) may result whenever carbon -rich materials undergo incomplete combustion. The mixture is also produced in volcanoes and forest fires, and is also a component of cigarette smoke and is a principal component of combustion products produced by the burning of PVC (polyvinyl chloride). The principal method for obtaining BTX industrially is the catalytic reforming process. Catalytic Reforming was first used in the 1940's (Fahim, M. A. 1990). This process accounts for 30% of the world's BTX production. Catalytic reforming involves the dehydrogenation of Naphthenes and gasoil to aromatics, or the isomerization of alkylnaphthenes and the dehydrogenation of them. Paraffins are also dehydrocyclized to aromatics, but the reaction is slow. (Schleyer, Paul von Ragué. 2001)

## 2.4.1 Benzene

Is an organic chemical compound with the molecular formula  $C_6H_6$ . The word "benzene" derives historically from "gum benzoin", sometimes called "Benjamin", an aromatic resin known to European pharmacists and perfumers since the 15th century as a product of Southeast Asia. The hydrocarbon derived from benzoic acid thus acquired the name benzin, benzol, or benzene. Benzene is a component of petroleum, typically around 3 per cent by mass (Axens, 2002).

It is an organic chemical compound with the molecular formula  $C_6H_6$ . It is sometimes abbreviated Ph-H. Benzene is a colourless and highly flammable liquid with a sweet smell. Because it is a known carcinogen, its use as an additive in gasoline is now limited, but it is an important industrial solvent and precursor in the production of drugs, plastics, synthetic rubber, and dyes. Benzene is a natural constituent of crude oil, and may be synthesized from other compounds present in petroleum (Schleyer, 2001).

### 2.4.1.1 Discovery and history

The word "benzene" derives historically from "gum benzoin", sometimes called "Benjamin" (i.e., benzoin resin), an aromatic resin known to European pharmacists and perfumers since the 15th century as a product of Southeast Asia. "Benzoin" is itself a corruption of the Arabic expression "luban jawi," or "frankincense of Java." An acidic material was derived from benzoin by sublimation, and named "flowers of benzoin," or benzoic acid. The hydrocarbon derived from benzoic acid thus acquired the name benzin, benzol, or benzene (King, 1981).

Michael Faraday first isolated and identified benzene in 1825 from the oily residue derived from the production of illuminating gas, giving it the name *bicarburet of hydrogen*. In 1833, Eilhard Mitscherlich produced it via the distillation of benzoic acid (from gum benzoin) and lime. Mitscherlich gave the compound the name *benzin*. In 1836, the French chemist August Laurent named the substance "phène"; this is the root of the word phenol, which is hydroxylated benzene, and phenyl, which is the radical formed by abstraction of a hydrogen atom (free radical  $H^*$ ) from benzene (Mukhopadhyay, 1991).

In 1845, Charles Mansfield, working under August Wilhelm von Hoffman, isolated benzene from coal tar. Four years later, Mansfield began the first industrial-scale production of benzene, based on the coal-tar method (Mukhopadhyay, 1991).

#### 2.4.1.2 Uses

**Early uses:** In the 19th and early-20th centuries, benzene was used as an after-shave lotion because of its pleasant smell. Prior to the 1920s, benzene was frequently used as an industrial solvent, especially for degreasing metal. As its toxicity became obvious, benzene was supplanted by other solvents, especially toluene (methyl benzene), which has similar physical properties but is not as carcinogenic (Schleyer, 2001).

In 1903, Ludwig Roselius popularized the use of benzene to decaffeinate coffee. This discovery led to the production of Sanka (the letters "ka" in the brand name stand for *caffeine*). This process was later discontinued. Benzene was historically found as a significant component in many consumer products such as Liquid Wrench, several paint strippers, rubber cements, spot removers and other hydrocarbon-containing products.

As a gasoline (petrol) additive, benzene increases the octane rating and reduces knocking. As a consequence, gasoline often contained several percent benzene before the 1950s, when tetraethyl lead replaced it as the most widely-used antiknock additive. With the global phase-out of leaded gasoline, benzene has made a comeback as a gasoline additive in some nations. In the United states, concern over its negative health effects and the possibility of benzene's entering the groundwater have led to stringent regulation of gasoline's benzene content, with limits typically around 1%. European petrol specifications now contain the same 1 % limit on benzene content. The United States Environmental Protection Agency has new regulations that will lower the benzene content in gasoline to 0.62 % in 2011 (Schleyer, 2001).

**Current uses:** Today, benzene is used mainly as an intermediate to make other chemicals. Its most widely-produced derivatives include styrene, which is used to make polymers and plastics, phenol for resins and adhesives (via cumene), and cyclohexane, which is used in the manufacture

of Nylon. Smaller amounts of benzene are used to make some types of rubbers, lubricants, dyes, detergents, drugs, explosives, napalm, and pesticides.

In both the US and Europe, 50 % of benzene is used in the production of ethylbenzene/styrene, 20 % is used in the production of cumene, and about 15 % of benzene is used in the production of cyclohexane (eventually to nylon).

#### **2.4.1.3 Health effects**

Benzene exposure has serious health effects. The American Petroleum Institute (API) stated in 1948 that "it is generally considered that the only absolutely safe concentration for benzene is zero." The US Department of Health and Human Services (DHHS) classifies benzene as a human carcinogen. Long-term exposure to excessive levels of benzene in the air causes leukaemia, a potentially fatal cancer of the blood-forming organs, in susceptible individuals. In particular, Acute Myeloid Leukaemia or acute non-lymphocytic Leukaemia (AML and ANLL) is not disputed to be caused by benzene. IARC rated benzene as "known to be carcinogenic to humans" (Group 1).

The short-term breathing of high levels of benzene can result in death; low levels can cause drowsiness, dizziness, rapid heart rate, headaches, tremors, confusion, and unconsciousness. Eating or drinking foods containing high levels of benzene can cause vomiting, irritation of the stomach, dizziness, sleepiness, convulsions, and death.

The major effects of benzene are manifested via chronic (long-term) exposure through the blood. Benzene damages the bone marrow and can cause a decrease in red blood cells, leading to anaemia. It can also cause excessive bleeding and depress the immune system, increasing the chance of infection. Benzene causes leukaemia and is associated with other blood cancers and pre-cancers of the blood.

Some women having breathed high levels of benzene for many months had irregular menstrual periods and a decrease in the size of their ovaries. Benzene exposure has been linked directly to the neural birth defects spina bifida and anencephaly. Men exposed to high levels of

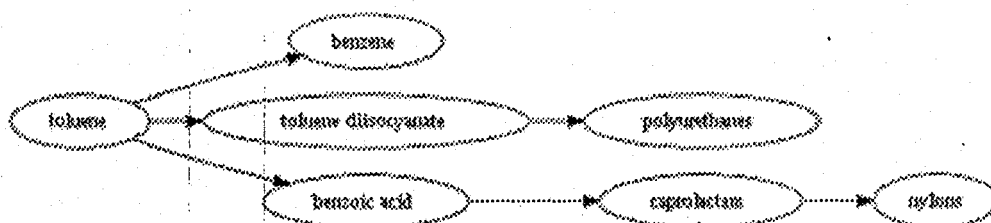
benzene are more likely to have an abnormal amount of chromosomes in their sperm, which impacts fertility and fetal development (Speight, 1999).

## 2.4.2 Toluene

Is another aromatic compound with a molecular formula  $C_7H_8$ . Toluene is a colourless hydrocarbon, occurring in coal tar, specific gravity 0.86, boiling point  $110.6^\circ C$  ( $231.1^\circ F$ ). Toluene is sometimes called toluol or methylbenzene. The name *toluene* reflects the way in which it was once prepared, through destructive distillation of balsam of tolu. A great deal of industrial toluene is prepared in oil refineries by the alkylation of benzene. It is used as a solvent and as a source of synthetic compounds, for example, in the production of trinitrotoluene. Prolonged breathing of toluene vapour is harmful and should be avoided (Speight, 1999).

### 2.4.2.1 Uses

Chemicals produced from toluene are schematically represented below;



**Toluene** - methylbenzene; can be a solvent or precursor for other chemicals

**Toluene diisocyanate (TDI)** - used as co-monomers with diols or polyols to form polyurethanes or with di- or polyamines to form polyureas

**Polyurethanes** - a polymer formed from diisocyanates and diols or polyols

**Benzoic acid** - carboxybenzene

**Caprolactam, nylon** (Clause, 1998).

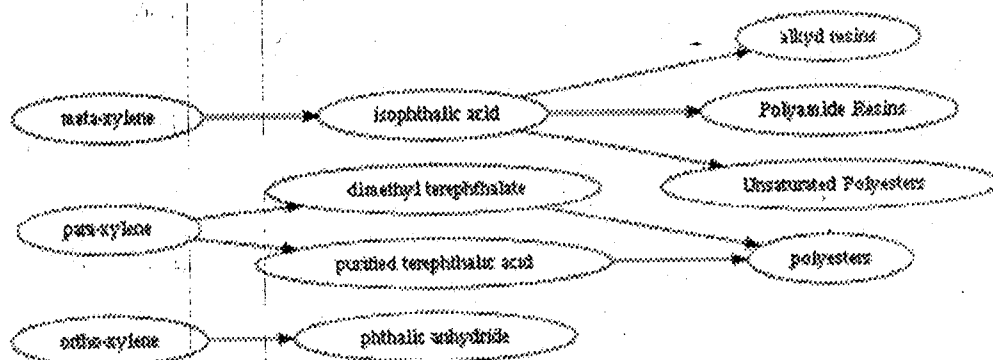


### 2.4.3 Xylene

This hydrocarbon has the molecular formula  $C_8H_{10}$ . Not much literature is available on this chemical aromatic compound. The main information to be known is that it is a derivative of the benzene compound, as shown by its ring formula shown above (James, 2001).

#### 2.4.3.1 Uses

Chemicals produced from xylenes are represented below;



**Mixed xylenes** - any of three dimethylbenzene isomers, could be a solvent but more often precursor chemicals

**Ortho-xylene** - both methyl groups can be oxidized to form (*ortho*-) phthalic acid

**Para-xylene** - both methyl groups can be oxidized to form terephthalic acid

**Dimethyl terephthalate** - can be copolymerized to form certain polyesters

**Polyesters** - although there can be many types, polyethylene terephthalate is made from petrochemical products and is very widely used.

**Purified terephthalic acid** - often copolymerized to form polyethylene

**Terephthalate, Polyesters, Meta-xylenes, Isophthalic acid, Alkyd Resins, Polyamide Resins,**

**Unsaturated Polyesters, Phthalate anhydride** (Clause, 1998).

## **2.5 Production of BTX from the Cracking of Gasoil**

This project work is mainly concerned with the cracking of gasoil to produce BTX. This is not a new procedure. For the objectives of the project to be met, the best cracking method will have to be found. From the diligent research already conducted, the procedure for carrying out the experiment for this project has been found. Further details on this procedure and materials/equipments involved are shown in the preceding chapter.

## **CHAPTER THREE**

### **3.0 METHODOLOGY**

In this chapter, priority is placed on the collection and gathering of all the required materials and equipment necessary for carrying out the research experiment. Emphasis is also placed on the experimental procedures used.

#### **3.1 Materials and Equipments**

A list of all materials and equipments used in carrying out the experiment is shown in the following tables below.

**Table 3.1 List of Materials Used**

Name	Research Code Name	Source	Comments
Heavy Gas Oil	HGO	KRPC	As main feedstock for the cracking reaction.
Alumina-Silicate Molecular Sieve Catalyst	Zeolite	KRPC	Applied to the reaction in appropriate ratios in order for the cracking reaction to occur.
Powdered Zinc Metal	Zn	Panlac Nigeria Ltd, Minna	Necessary for Hydrogen Production
Concentrated Hydrochloric Acid	HCL	Panlac Nigeria Ltd, Minna	Necessary for Hydrogen Production
Epoxy Sealant Resin	Epoxy	Panlac Nigeria Ltd, Minna	For Proper sealing of equipments used, to avoid interactions with external influences
Distilled Water		Panlac Nigeria Ltd, Minna	For mixing, topping and other water necessitating purposes
Glycol solvent	Glycol	Panlac Nigeria Ltd	For separating the aromatic mixture from reformat

**Table 3.2: List of Equipments Used**

Name	Source	Comments
Reactor vessel	Sourced for, and fabricated at Science Equipment Development Institute (SEDI)	Main reaction chamber, where cracking occurs
Condenser	Chemical Engineering laboratory	For condensing vapours to liquids
Retort stands	Water, Aquatic and Fishery Technology laboratory, (WAFT)	Used for holding other equipments in place
Connecting tubes	Panlac Nigeria Ltd, Minna	For transferring feed, products, etc in the setup
Heating mantle	Personal property	Main source of heat for heating up the experiment
Separator	Panlac Nigeria Ltd, Minna	For separating vapour from liquid constituents
Flat bottomed flasks	WAFT	For holding liquid materials during the experiment
Pressure gauge	Panlac Nigeria Ltd, Minna	For gauging the reaction pressure

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Thermometer	Panlac Nigeria Ltd, Minna	For gauging the reaction temperature
Corks	Panlac Nigeria Ltd, Minna	Acts as stopper, not allowing materials to escape
Weighing balance	WAFT	For weighing the experiment samples
Gas masks	Panlac Nigeria Ltd, Minna	Facial protective gear against toxic gases
Oven	WAFT	Heating under predetermined conditions
Beakers	WAFT	For measurement and heating purposes

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## 3.2 Experimental Procedures

All experiments carried out in this research project are fully covered in this section including detailed description of the procedures taken.

### 3.2.1 Catalytic cracking of Heavy Gas Oil to Produce BTX

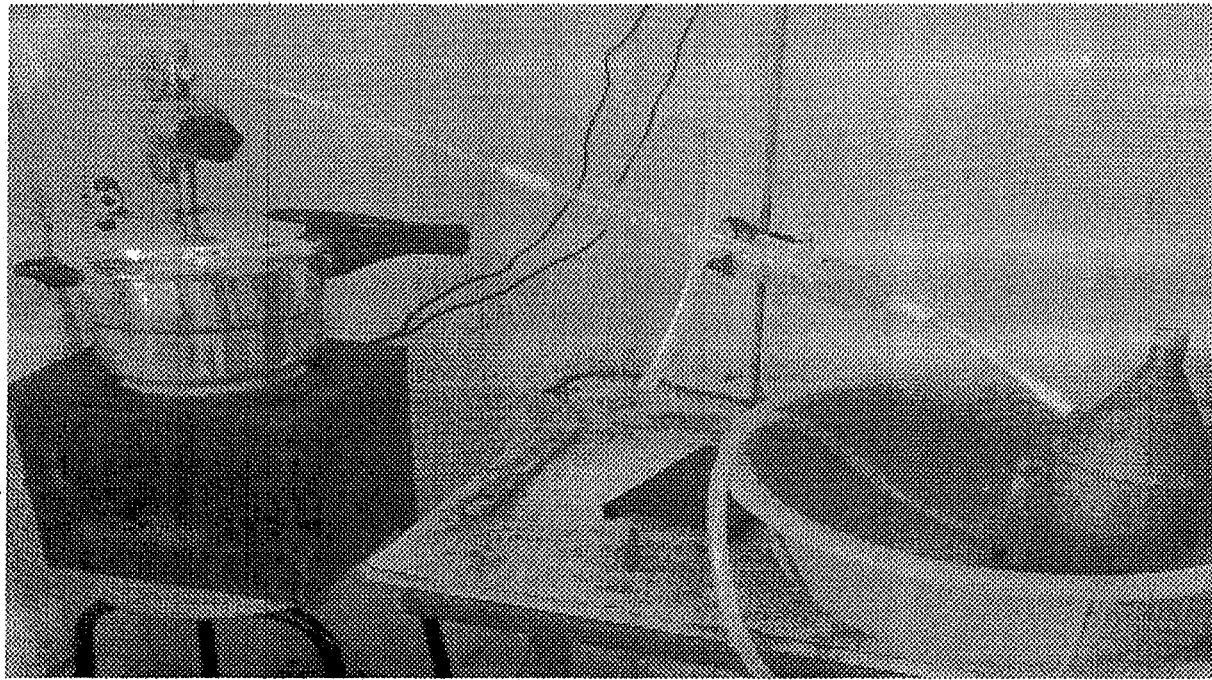
The production of BTX from the heavy gas oil feedstock was a two stage process. The first stage involved the cracking of the gas oil to produce naphtha. On the other hand, the second stage is the cracking of the naphtha produced to obtain the reformat from which the desired BTX product is obtained. Interestingly, between these two processes is the production of Hydrogen gas which was utilized in the second stage of the process when the naphtha was reformed in order to obtain reformat. When the reformat was finally obtained, solvent extraction was used in obtaining the BTX component from it. This is the last stage of the experiment.

### 3.2.2 Fluid Catalytic Cracking of Heavy Gas Oil to Produce Naphtha (First Stage)

2.3 litres of the heavy gas oil was measured using a measuring cylinder and then transferred into a beaker which was then placed in an electric oven. The temperature of the oven was set to a value of 450 ° C and then allowed to heat up. Whilst, the Gas oil was heating, the powdered Zeolite catalyst was put into the reactor vessel and securely sealed up. The amount of catalyst measured into the reactor was 100 g. The reactor was placed on the heating mantle and also allowed to heat up. After a time period of about 2 hours, the Zeolite catalyst was noted to have heated to the desired temperature of 700 ° C. At this point, the gasoil feed, which had also been heated to 450 ° C, was removed from the oven and then manually transferred into the reactor vessel via a glass funnel placed in an opening on the reactor vessel. When the hot gas oil got in contact with the hotter catalyst powder in the reactor space, the cracking reaction then occurred. The products produced were let out via connecting glass cylinders into the condenser where the reaction temperature was reduced considerably.

The liquid-vapour mixture of products was then allowed to flow from the condenser into the metallic separation chamber which was improvised to also act as a distillation chamber. The

separation chamber with the products in it was put into a cold water bath were further cooling occurred, causing more of the vapour products to condense in the separator. After 45 minutes of cooling, the separator was transferred to the heating mantle and the heat supply was turned on. The separator vessel was heated continuously on the mantle until individual vapour products were noticed to be exiting through the opening in the vessel but none of the vapours were collected. The temperature of the vessel was continuously monitored until it was noted to have approached a value approximate to that in the boiling point range of heavy naphtha, which is between  $90^{\circ}\text{C}$  and  $200^{\circ}\text{C}$ . At this point, a connecting tube was attached to the lone opening in the separator, and the naphtha vapour produced was siphoned via the glass condenser (where cooling occurred) into a gas collection bottle placed in a cold water bath (for further cooling). When the naphtha produced had cooled to room temperature, it was securely packaged and made ready for the next step in the experiment.



**Figure 3.1** Experimental setup for the cracking of Gas oil to produce Naphtha. Insert are the reactor vessel upon the heating mantle. Also are the condenser tube and then the separator vessel placed in a cold water bath.

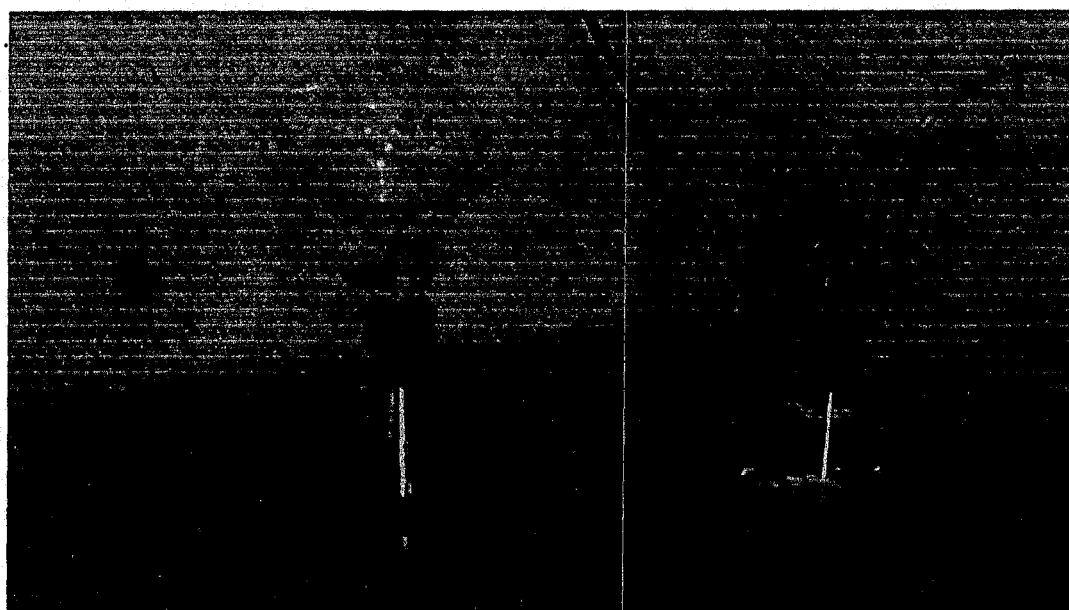
### 3.2.3 Procedure for Hydrogen Production

Two flat bottomed flasks were arranged in the configuration shown below (Figure 3.1). The first flask was first washed and thoroughly rinsed out with distilled water and dried. It was then



covered using a cork in which two holes had been previously bored. A glass funnel flask and a hollow glass rod were then inserted into the two holes, respectively. The second round bottomed flask was put through the same procedure as the first, except that two hollow glass rods were inserted into the holes drilled in the corks.

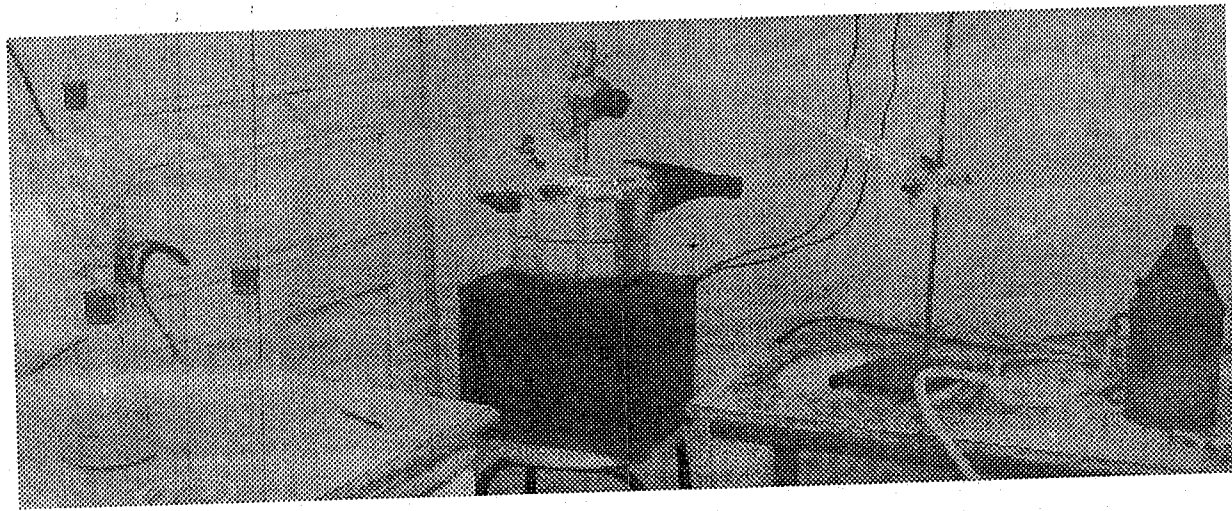
The two flasks were placed side by side and the connecting tubes were used to connect one to the other. 30 g of granulated Zinc powder was then measured and poured into the first flask. The second flask was filled to the neck line with distilled water and securely corked. 30 cm<sup>3</sup> of concentrated Hydrochloric Acid was measured out into a beaker, and then it was diluted using 120 cm<sup>3</sup> of distilled water. The diluted acid was then transferred into the first flask via the glass funnel placed in it. As the acid slowly mixed with the zinc in the flask, Hydrogen was produced. The Hydrogen produced was then passed through distilled water contained in the second flat bottomed flask, in order to remove any impurities contained in it. The purified Hydrogen was finally transported through the connecting tubes into the reactor where it was used for hydrogenation purposes during the naphtha reforming process.



**Figure 3.2** Experimental setup for Hydrogen production. Insert are the two flat bottomed flasks containing the Zinc powder and distilled water respectively. Also is the glass funnel through which the diluted acid is poured into the first flask.

### 3.2.4 Catalytic Reforming of Naphtha to Obtain Reformate

The naphtha produced from the initial cracking of the heavy gas oil feedstock was put into a metallic container and then placed inside the heating oven and allowed to heat up to about 200 °C. While it heated, preparations were also being made for the production of hydrogen gas as fully described in Section 3.2.3. 90 g of Platinum catalyst was then measured and placed inside the reactor. When the naphtha had heated up to the desired temperature, it was removed from the oven and transferred into the reactor vessel and sealed perfectly. At this point, the Hydrogen produced was also transferred into the reactor and allowed to mix with the naphtha feed. The heating element upon which the reactor was placed was then turned on and the cracking reaction within the reactor vessel was allowed to proceed accordingly. The thermometer readings were constantly observed, and at a temperature of about 450 °C, vapour products were seen to be exiting the reactor. The vapours produced were passed through a condenser and into the separator vessel in which the gas fractions were let out while the liquid fraction (almost pure reformate) was collected. After the reformate had cooled considerably, and the reactor was free of all initial naphtha, the same process described above was repeated on the reformate produced. When the second reformate was obtained from the repeated process and all unneeded gases had been let out, it was cooled and then prepared for the next stage of the experiment.



**Figure 3.3** Experimental setup for naphtha reforming process. Insert, is the Hydrogen production section from which Hydrogen is led into the reactor vessel containing the Naphtha being cracked. Also, are the condenser and separator vessel.

### 3.2.5 Solvent Extraction of Aromatic Components (BTX)

The solvent used for extracting the aromatic components present in the reformat produced from the last stage was glycol. The glycol was placed in a beaker and then the reformat was poured into it and mixed completely by stirring it. After a period of time, a boundary was noticed to have formed. The upper layer formed was then decanted into another beaker. The lower portion of the decanted (the raffinate) was then kept apart, while the upper portion containing the aromatics was then used further. A round bottom flask was then filled with water and placed upon the heating mantle to heat up. When steam was produced, it was passed via rubber tubes through the beaker containing the aromatics in order to remove other hydrocarbons present in the BTX solution mixture. The steam was passed continuously for about 30 minutes and then disengaged. The mixture left in the beaker was then sent to the separation (distillation) vessel and heated vigorously till separation of Benzene, Toluene and Xylene was achieved. The separated sample was then tested to confirm conformance with known BTX standards.

## CHAPTER FOUR

### 4.0 RESULTS AND DISCUSSIONS

#### 4.1 Results

The experiment had to do with the production of Benzene, Toluene and Xylene (BTX) from gas oil feedstock. The work does not involve the computation or derivation of data.

After all materials and equipments had been purchased and setup for the experiment, the process began with the production of Hydrogen gas. This part of the experiment was a success because Hydrogen gas was duly produced. The hydrogen produced was noted to have physical properties consistent with that for standard Hydrogen properties. The gas produced was an odourless, colourless and tasteless gas, properties that are commiserate with standard physical properties of Hydrogen gas. The hydrogen gas was produced for the experiment for three major purposes, these include;

- Hydrotreating of the naphtha in the second stage of the experiment to remove all sulphur present in the naphtha (hydrodesulphurization).
- The dehydrogenation of the naphthenes present in the naphtha to convert them into aromatics.
- The dehydrogenation and aromatization of the Paraffins present in the naphtha to aromatics (dehydrocyclization)

The hydrogen production aspect of the experiment was therefore a huge success, since the gas was duly produced.

When the hydrogen gas had been produced and was being fed into the reactor containing the naphtha and catalyst, an explosion occurred. This explosion was quite huge and led to the destruction of materials and equipments being used for the experiment. The reactor vessel, heating mantle, pressure gauge, and several other equipments were all destroyed in the blast. Added to this was also damage that was done to the immediate environment via fire and smoke. Fortunately, no harm was done to any human.

Owing to the blast, the experiment could not be continued. The cracking of the gasoil and the reforming of the naphtha had to be stopped due to the loss of the reactor and the heating mantle during the blast. Furthermore, due to the unavailability of fresh funds to undertake the fabrication of a new reactor and heating mantle, the experiment had to be suspended, and the results obtained until the time of the blast presented duly.

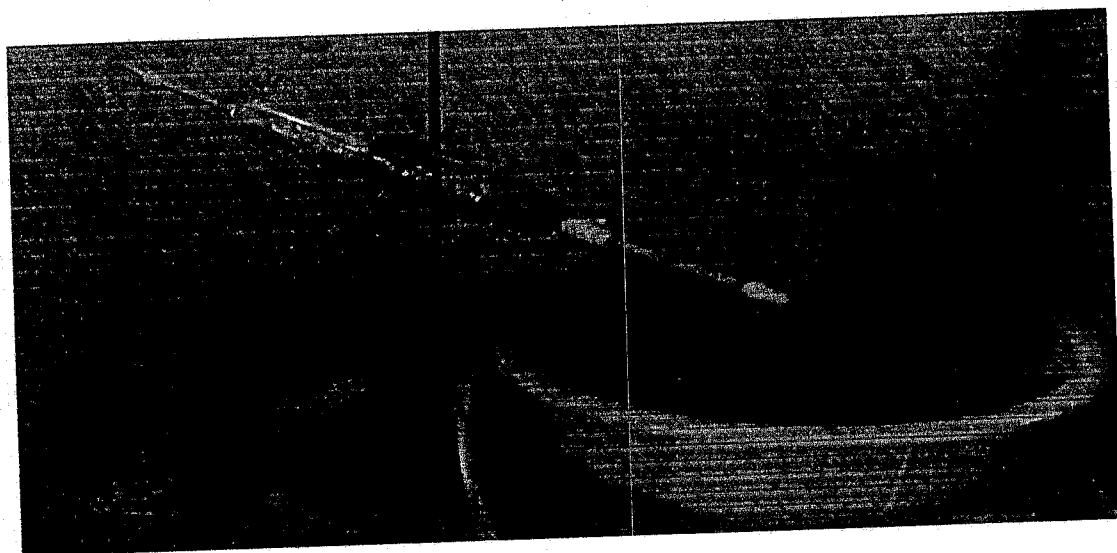
Below are pictures showing the results of the experiment cum the explosion. Also, after due analysis and investigations, the reasons for the occurrence of the blast were found and will be discussed in detail in the next section.



**Figure 4.1 Destroyed heating mantle**



**Figure 4.2 Destroyed reactor and heater**



**Figure 4.3 the experimental setup after the explosion. Insert are the condenser and separator vessel.**

## 4.2 Discussion of Results

At the end of the experiment, the projected results as expected were not obtained. The experiment was only partly a success. Said success was attained in the production of Hydrogen gas. As has already been elaborated in the results obtained, the gas produced was found to be Hydrogen, due to its consistency with known standards.

The other aspects of the experiment turned out to be quite disastrous. This was mainly due to the huge explosion that occurred in the course of the experiment. Most of the materials and equipments used for the experiment were purchased from external sources, while some others which were quite hard to lay hands on had to be fabricated. The process of fabricating these equipments was quite a grueling one because extensive research had to be done for the type of engineering materials to be used, the source of the materials, dimensions for production and the production process. The main equipment that needed to be fabricated was the reactor vessel with all other utilities attached to it (pressure gauge, thermometer, etc). After diligent research, the reactor was settled to be built using stainless steel as the raw material. This piece of information was relayed to the Science Equipments Development Institute (SEDI) Minna, who had been chosen to produce the equipment for the experiment. Feedback was received from SEDI that building the reactor vessel from stainless steel was going to be impossible since the raw materials for such a venture (stainless steel) and the machinery for the production were totally unavailable at the time. SEDI then proposed Aluminum as an alternative to stainless steel for the design of the reactor vessel. After long periods of discussions and persuasions as to its strength and viability for the experiment, it was agreed that the reactor be built (a decision that was greatly favoured considering the lack of time).

Again, during the course of carrying out the experiment, the reactor exploded. After due investigation and analysis, the cause of the explosion was determined to be due mainly to the build up of pressure within the reactor vessel and the inability of the reactor to contain the high pressure. Another factor determined to have also played a part in the cause of the explosion was the nature of the materials being heated (naphtha and hydrogen). At the start of the experiment, the naphtha and catalyst were fed into the reactor and then set upon the heating mantle. At that

point, the temperature and pressure were at their minimum values. As time elapsed, the temperature started to increase as well as the pressure. When the temperature reached approximately 140°C, the pressure was still within acceptable limits. When the temperature got to 146°C, the reactor exploded. It was this explosion that led to the destruction of the equipment being used. It can be concluded therefore that the explosion occurred due to excess pressure within the reactor and the explosive nature of the materials being heated.

#### **4.2.2 Discussion of Expectations at the End of the Experiment**

Had the explosion not occurred, the aromatics Benzene, Toluene and Xylene (BTX) were expected to be obtained at the end of the experiment. The process of achieving this is detailed in chapter 3. The BTX produced was expected to have properties commiserate with that for standard BTX stated in the literature review (Chapter 2).

Had a final product been obtained, it would have been comprehensively analyzed to confirm whether it is BTX. The process of testing for BTX has already been discussed in chapter 3.

## CHAPTER FIVE

### 5.0 CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

At the end of this research work, the aims of carrying out the experiment were partly achieved. It is thus concluded herein that the project work was quite successful.

The results obtained from the experiment show that in the process of producing BTX, the reactor exploded, leading to the loss of equipments and materials. This huge setback led to the inability to see the experiment to completion. Proper analysis of the cause of the explosion was done. Excess pressure build up within the reactor, as well as the inability of the reactor to contain the pressure and also the explosive nature of the naphtha and hydrogen mixture in the reactor were cited as reasons why the explosion occurred. The material choice for the fabrication of the reactor (aluminium) was then also stated as a mitigating factor as to why the blast happened.

On the other hand, Hydrogen production for the purpose of catalytically cracking the naphtha that was to be obtained was successful. The gas produced was analyzed to confirm that it was Hydrogen.

#### 5.2 Recommendations

It was observed during the course of carrying out the experiment for this research work that there was either a short supply or a complete unavailability of many equipment and/or materials necessary to get the work done. This led to the sourcing of such materials and equipment from other places at great cost. It is therefore of paramount interest to recommend herein that the laboratory be stocked fully with all necessary materials needed in order to carry out further experiment. Doing this, will go a long way in eliminating catastrophic incidents such as the explosion that occurred during this project as well as save time and money.

It is also highly recommended that experiments that pose great risk of explosion and/or becoming a danger to humans should be carried out under a very safe environment. Laboratories should therefore be properly fitted with emergency gears such as fire extinguishers and smoke



outlets and also quick escape routes for times of emergencies. Safety protocols for emergency situations should be eligibly printed and placed at vantage points within the premises of the laboratory.

Because of the explosion that occurred, it is hereby recommended that appropriate steps be taken to eliminate such. These steps include the use of certified reactors, heating mantle, etc. the use of equipments that can withstand great pressures and high temperatures will lead to great advancement in this research topic.

The reactor used for the experiment for the research project was not properly observed during the course of the experiment. The temperature and pressure gauges fitted to it were not duly monitored to be able to gauge the reaction conditions accurately. It is recommended therefore that great effort must be put into equipping reactors for consequent studies with proper and working control mechanisms. Also, such control mechanisms should be diligently monitored to avoid the reaction conditions going above limit. This will go a long way in eliminating scenarios of explosion.

The reactor used for the experiment was made of aluminium. When the pressure increased due to the reaction, the reactor was not strong enough to hold or contain the pressure. The reactor material therefore played a huge part in the blast. It is necessary to therefore recommend that further work should include finding a better alternative to using aluminium made reactor. Diligent investigation is advised and testing of any selected material is greatly recommended. For a start, it is recommended that the reactor material be made from stainless steel.

Further research into the 'cracking of gas oil to produce BTX' should be conducted. Such a study should include ways of improving on the process, best engineering materials to be used in conducting the experiment, etc. Note should be taken of the parameter(s) that could be manipulated during the production process in such a way that its efficiency is improved upon.

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## APPENDIX

### Calculation for the amount of catalyst required for the FCC cracking of the Gasoil feed

The amount of Gasoil feed used in carrying out the experiment for this research work was taken to be 2.3 litres. The ratio of the volume of Gasoil feed needed to the amount of catalyst required is given as 2 to 20. A value of 17 was chosen. (Chakka, 1994)

$$\frac{\text{volume of Gasoil}}{\text{volume of catalyst}} = 17$$

Volume of Gasoil used for the experiment = 2.3 litres =  $2300\text{cm}^3$

$$\frac{2300\text{cm}^3}{\text{volume of catalyst}} = 17$$

$$\text{Volume of catalyst} = \frac{2300\text{cm}^3}{17} = 133\text{ cm}^3$$

$$\text{Bulk density} = \frac{M_c}{V_c}$$

Where bulk density =  $0.75\text{ g/cm}^3$

$M_c$  = bulk density x volume of catalyst

$$M_c = 0.75 \times 133\text{ cm}^3$$

Mass of catalyst required for Gasoil cracking = 100 g

### Calculation for the quantity of catalyst required for Naphtha hydrogenation

The ratio of the volume of naphtha needed to the amount of catalyst required is given as being between 0.15- 15 (Chakka, 1994). If the ratio for this experiment is taken to be 15, then;

$$\frac{\text{volume of naphtha}}{\text{volume of catalyst}} = 15$$

Volume of naphtha used for the experiment = 1.8 litres

$$\frac{1800\text{cm}^3}{\text{volume of catalyst}} = 15$$

$$\text{Volume of catalyst} = \frac{1800 \text{ cm}^3}{15} = 120 \text{ cm}^3$$

$$\text{Bulk density} = \frac{M_c}{V_c}$$

$$\text{Where bulk density} = 0.75 \text{ g/cm}^3$$

$$M_c = \text{bulk density} \times \text{volume of catalyst}$$

$$M_c = 0.75 \times 120 \text{ cm}^3$$

$$\text{Mass of catalyst required for Naphtha hydrogenation} = 90 \text{ g}$$

### Quantity of hydrogen chloride required for Hydrogen production

Using 30g of zinc

30 g Zn	72.92 g HCL
<hr/>	
	65.4 g Zn

$$= 33.45 \text{ g HCL}$$

$$\text{Density} = 1.18 \text{ g/cm}^3$$

$$\text{Volume of HCL} = \text{Mass} / \text{Density}$$

$$\text{Volume of HCL} = \frac{33.45}{1.18}$$

$$= 28.35 \text{ cm}^3$$

### Quantity of hydrogen produced



30 g of zinc was measured and used for the experiment

Converting, using the above stoichiometry, we obtain;

$$\begin{array}{c|c} 30 \text{ g Zn} & 2 \text{ g H}_2 \\ \hline & 65.4 \text{ g Zn} \end{array}$$

$$= 0.917 \text{ g of H}_2$$

$$\text{Volume} = \frac{\text{mass}}{\text{density}}$$

where the density of Hydrogen is  $= 0.0000886 \text{ g/cm}^3$

$$\text{Volume} = \frac{1.52 \text{ g}}{0.0000886 \text{ cm}^3}$$

$$= 10.35 \times 10^3 \text{ cm}^3$$

Volume of hydrogen produced = 10.35 litres

The ratio of hydrogen to naphtha for this experiment is 2:1 to 10:1. A ratio of 10:1 was chosen

for this research work. The reason for this choice is because the more the increase in the

Hydrogen to feed ratio, the more likely it is for more sulphur to be removed. (De Almeida, 2010)