

**DETERMINATION OF THE OPTIMUM
CONVERSION OF CATALYTIC CRACKING OF
BUTANE IN A FLUIDIZED BED REACTOR**

BY

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DECLARATION

I hereby declare that Mr. John Sunday Oluwarotimi wrote and carried out this project and that the contents are the investigation and result of my model and calculations.

Information obtained from published or unpublished works of other have been well acknowledged by means of references and to the best of my knowledge it has never been presented in any seminar, symposium or else where in any form for the award of diploma or degree.

John Sunday Oluwarotimi



Sign.

3/11/2003

Date

CERTIFICATION

I hereby certify that this project titled "Determination of the optimum conversion of the catalytic cracking of butane in a fluidized bed reactor" was carried out by John Sunday Oluwarotimi under the supervision of Engr M.A. Olutoye, Department of Chemical Engineering, Federal University of Technology Minna, Niger State.



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DATE

EXTERNAL EXAMINER

DATE

DEDICATION

This project is dedicated to my saviour, Jesus Christ, in whom I live, move and

make my being

ACKNOWLEDGEMENT

My utmost gratitude goes to God Almighty who has not left me unto myself but has perfected what He began.

My profound gratitude goes to my beloved father, Pa H.O John, who stood by me in all ramifications. I say thanks in a million for being a father. Much appreciation goes to my sister, Ronke who has contributed immensely to what I am today.

I will not forget to say a big thank you to God-sent brothers, Mr. Suraju and Mr. Gbenga Oguntope who had invested so much in seeing my success in life. May God reward you abundantly.

My thank also goes to my fellowship (TACSFON) brethren who responded to God in contributing their human-pillar effort. Your memory will always be fresh in my heart.

I like to specially thank my friends and room mates, especially brothers like Dayo, Isaac, Alan, Kayode, and Sunday. It's indeed a privilege of God to have come across some one like you. I will also like to appreciate my supervisor, Engr M. A. Olutoye for his encouragement guidance and care. May God bless you.

And to all wise-hearted men who have made this world a worth living. I say thanks

ABSTRACT

The research work was carried out to determine the optimum conversion and optimum operating condition of the catalytic cracking of butane in a fluidized reactor. To achieve this, an experiment was carried out using a prototype fluidized bed reactor. Different measured weights of catalyst (W_{cat}) were charged into the reactor. The butane from the cylinder was allowed to flow at different flowrate. Heat was applied until a temperature range of 40 – 60⁰C and 60 – 80⁰C were obtained. Six different runs of results i.e. three from each range of temperature were obtained. The products obtained were collected into a vessel containing an organic solvent, petroleum ether.

A gas chromatograph was then used to analyze the result of each runs.

From the experimental result the optimum conversion was calculated by plotting the graph of conversion, X_A and temperature, T. Optimum conversion and temperature was taken to be average equilibrium conversion and temperature within the range of temperature.

Consequently, an optimum conversion and temperature of 63.3%, 43.7⁰C within the temperature range of 40 - 60 ⁰C, while an optimum conversion and temperature of 71.5%, 62.5 ⁰C were obtained within a temperature range of 60-80⁰C respectively.

NOMENCLATURE

C_A = concentration at the outlet point

C_{A0} = initial concentration

W_{cat} = weight of catalyst

r_A = rate of disappearance of A

g = acceleration due to gravity

X_A = conversion of the reactants used

X_{op} = optimum conversion

T_{eq} = equilibrium temperature

T_{op} = optimum temperature

F_{A0} = molar flow rate

X_{eq} = equilibrium conversion

V = flow rate

NOMENCLATURE

LIST OF FIGURES

- Fig 2.4.3 Fluidized bed behavior
- Fig 2.5.2 A detailed reaction scheme for catalytic cracking of paraffins
- Fig 3.1 Sketch of a laboratory fluidized bed catalytic reactor.
- Fig 4.1a Graph of rate of reaction Vs concentration for 1st run
- Fig 4.1b Graph of rate of reaction Vs concentration for 2st run
- Fig 4.1c Graph of rate of reaction Vs concentration for 3rd run
- Fig 4.1d Graph of rate of reaction Vs concentration for 4th run
- Fig 4.1e Graph of rate of reaction Vs concentration for 5th run
- Fig 4.1f Graph of rate of reaction Vs concentration for 6st run
- Fig 4.1g Graph of $\ln K$ Vs inverse of temperature.
- Fig 4.1h Graph of conversion Vs temperature.

TABLE OF CONTENTS

Title page	i
Declaration	ii
Certification	iii
Dedication	iv
Acknowledgement	v
Abstract	vi
Nomenclature	
Table of contents	vii
CHAPTER ONE	1-5
1.0 Introduction	1
1.1 Aims and Objectives	4
1.2 Scope of study	5
1.3 Limitation of the study	5
CHAPTER TWO	6-25
2.0 Literature review	6
2.1 Fluidized bed and its application	6
2.2 Catalytic cracking	7
2.3 Fluidized catalytic cracking	8
2.4 Fluidization	9
2.4.1 Advantages of fluidization	10
2.4.2 Disadvantages of fluidization	10
2.4.3 Gas-Solid fluidization	10
2.4.4 Terms used in Gas-Solid fluidization	12
2.4.4.1 Minimum fluidization velocity, U_{mf}	12
2.4.4.2 Minimum bubbling velocity, U_{mb}	14
2.4.4.3 Terminal velocity, U_t	14

2.4.4.4 Particle regime	15
2.5 Catalyst	17
2.5.1 Zeolites	17
2.5.1.1 Advantages of Zeolites catalyst.	18
2.5.2 Paraffin cracking	18
2.5.2 .1 Mechanism for cracking butane.	19
2.5.2.2 Rate of cracking	20
2.5.2.3 Coke formation	21
2.6 Process variable and optimization	22
2.6.1 Process variable	22
2.6.2 Process optimization	23
2.6.3 Kinetics of cracking	24
CHAPTER THREE	26-28
3.0 Experimental procedure	26
3.1 Experimental techniques	26
3.2 Diagram	27
3.3. Methodology	28
CHAPTER FOUR	29-37
4.0 Results and discussions	29
4.1 Experimental results	29
4.2 Calculation	31
4.3 Discussion of results	36

CHAPTER FIVE	38-39
5.0 Conclusion	38
5.1 Recommendation	39
Reference	40
Appendix A	41
Appendix B	42
Appendix C	43

CHAPTER ONE

1.0 INTRODUCTION

As the need for upgrading of high boiling fractions of hydrocarbons to high octane gasoline becomes a necessity, catalytic process becomes highly imperative and couples with the fact that catalytic cracking of some hydrocarbons crack faster than non-catalytic system. Catalytic cracking process is thereby preferred to old, archaic thermal cracking.

Today, the catalytic cracking unit in a modern refinery has without any doubt become the major process for producing gasoline range hydrocarbons from a long-chain higher boiling fractions of crude oil and product of coker unit

The fluid catalytic cracking (FCC) process is the central process in modern gasoline oriented refinery. This is so called because of the application of fluidization as regard the fluidized used.

In the United States refineries, the amount of feed processed by fluid catalytic unit (FCCU) is equivalent to 35% of the total crude oil processed. As of January 1991, installed FCCU capacity in the United States was $8.6 \times 10^5 \text{ m}^3 / \text{d}$ (5.4×10^6 barrels/d).

(9)

Although the FCCU has long been an important refinery processing tool in the United States, refinery gasoline demands outside the U.S have been satisfied largely from the gasoline naturally present in crude oil. This situation is changing, and the need for catalytic cracking is now growing steadily everywhere. Worldwide, excluding North America, Eastern Europe, and Mainland, China, installed FCCU capacity increased nearly 60% in the 10 years period from 1981 to 1991 and in 1991 stood at $7.3 \times 10^5 \text{ m}^3 / \text{d}$ (4.6×10^6 barrels/d)

(9)

Presently, by taking a closer look at the global need of quenching the thirst for propylene and propane shortage, reduction of worldwide liquidified petroleum gas (LPG) Consumption, absorption of excess butane, satisfaction of seasonal variation in demand propane, production polyethylene and polypropylene in a fluidized bed (which is the principal application of bed) and the likes. Butane, a paraffinic hydrocarbon, produced primarily in association with natural gas processing and certain refinery operation such as catalytic cracking reforming can also be catalytically converted in order to alleviate the aforementioned yearnings.

Consequently, this project tagged “DETERMINATION OF THE OPTIMUM CONVERSION OF CATALYTIC OF BUTANE IN A FLUIDIZED BED REACTOR” is set out to meet some of the demands highlighted above.

To this end, an applied knowledge of the catalytic cracking process, fluidization properties of the, kinetic study of the reaction taking place, optimization technique, e. t. c are hereby required so as to accomplish the target of the work.

Catalytic cracking process was developed from a discovery by Houdry in 1927. Houdry in his findings discovered that certain synthetic amorphous silica-alumina clays catalyzed the cracking of high molecular weight hydrocarbons to give a good yield of gasoline.

(9)

Though before then, industrial fluidized bed had begun with a large scale Winkler gasifier in 1926. And as of 1942, fluidized bed catalytic cracking (FCC) of crude oil to gasoline was commercialized.

(9)

However, the introduction of Zeolites into catalytic cracking in 1962, replaced the application of synthetic amorphous silica-alumina. This development revolutionized the cracking operation by virtue of selectivity to gasoline range hydrocarbon and their extremely high activity at least 10^4 times as active, when in hydrogen form, as the silica-alumina they replaced. Now the existing Zeolites are of various modifications. The most suitable modification chosen as far as catalytic cracking is concerned is the large pore Y Zeolites (Faujasites). This is chosen because of superior thermal and hydrothermal stability. They are commonly incorporated into what are called fluid catalytic cracking catalysts, or FCC catalysts.

The FCC process is highly complex but self-contained. It has been most widely used and today, it represents over 95% of all cracking plant. The basis of the FCC process is the fact that finely divided powders behave like a fluid when aerated with a gas.

In the FCC process, a bed of solid (catalysts) can be fluidized by a liquid or by a gas and liquid combinations. Liquid and gas-liquid fluidization applications are growing in number, but gas-solid fluidization dominates the fluidization field.

Gas-solid fluidization is the means by which a bed of solid is being leveled by a gas. Intense solids mixing and good gas-solid contact create an isothermal system having good transfer.

The reaction which occurs during catalytic cracking converts paraffin, alkyl naphthenes and alkyl aromatics to olefins plus shorter chain length paraffin, naphthenes, alkyl aromatic respectively.

Unlike the thermal cracking process, which involves a free radical chain reaction mechanism, catalytic cracking proceeds through the formation of carbonium. The kinetic study of the carbonium ion forms is the basis of all the reactions that occur in the catalytic cracking process.

As optimization is engineering and vice versa, an optimum determination of the process is required to enhance the efficiency of the process. For instance, to make optimum use of the high activity and selectivity of Zeolites, FCC catalysts utilize a largely inert silica-alumina support matrix, which acts to dilute the active Zeolites, provide a macro porous structure, and give the granular catalyst increased strength and resistance to abrasion. Without matrix Zeolites would lose selectivity by over cracking.

1.1 AIMS AND OBJECTIVES OF STUDY

Fluid catalytic cracking unit (FCCU) is aimed at producing gasoline from heavy oils, thereby increasing the ratio of light to heavy products from crude oil. Consequently large quantities of high octane gasoline and other valuable light products are produced.

However, in this unit the range of hydrocarbon types present is very diverse, thereby making the composition of the cracker feedstock complex. As a result of these, measurement of the exact hydrocarbon composition becomes difficult.

To this end, the aims and objectives of this project is to use a prototype plant needed for determining the optimum conversion of a single-typed paraffinic hydrocarbon (butane) in a fluidized bed reactor.

To accomplish these aims and objectives, some of these measures are taken:

- (i) Determining the optimum operating variable needed for the catalytic cracking process.

- (ii) Determining the fluidization properties and regenerating efficiency of the catalyst used.
- (iii) Determining the optimum condition favourable for the kinetic reaction taking place during carbonium ions formation.

1.2 SCOPE OF STUDY

The extent of study needed for determining the optimum conversion of a simple, gaseous alkanic molecule, butane in a fluidized bed reactor includes the following.

- (i) Physical and physiochemical study of the catalytic cracking of paraffin narrowing down to butane.
- (ii) Systematic and analytical study of the fluidized-bed design: a procedure which requires an understanding of particle properties.
- (iii) Catalytic coke and its effect on the feed being processed.

1.3 LIMITATION OF THE STUDY

Though fluid catalytic cracking process is self-contained, it is highly complex. Consequently this study will be restricted to operating variables and factors needed for determining the optimum conversion. Extension is the fluidization properties of the catalyst used, coupled with the physiochemical (kinetic) process taking place during the process. An elaborate study of the chemical process heat and mass transfer taking place will not be given.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 FLUIDIZED BED PROCESS AND ITS APPLICATION

This is the process employed extensively during catalytic cracking. The process is based on the fluidization properties of fine powders which enable continuous transportation of the catalyst between the reactor and regenerator at extremely high flow rates.

Other process employed in catalytic cracking includes the moving bed process. Here the catalyst is allowed to fall by gravity through the reactor and regenerator vessel before being transported mechanically to the top of the reactor. However from the processes developed so far, fluidized bed process has been the most widely used. It represents over 95 percent of all cracking plant.

Fluidized-bed catalytic cracking [FCC] of crude oil to gasoline is still the principal application of fine –powder fluidization. Industrial fluidized-bed applications began with a large- scale Winkler gasifier in 1926. The 1980s saw production of polypropylene in Fluidized bed.

Other newer areas of application were the production of semiconductor and ceramic material via chemical vapour deposition in a fluidized bed, and the use of liquid fluidized bed for biological application .

However, as of 1990s fluidized bed application may be separated into catalytic reaction, non –catalytic reactions and physical processes. The catalytic reaction typed includes

- Catalytic cracking of heavy petroleum fraction [FCC]
- Phthalic anhydride
- Acrylonitrile
- Aniline (hydrogenation of nitrobenzene)
- Synthesis of polyethylene and polypropylene.
- Fischer-Tropsch synthesis
- Oxidation of SO_2 to SO_3
- Chlorination or bromination of methane
- Maleic anhydride from butane
- Pyridine

2.2 CATALYTIC CRACKING

This is the process by which heavy hydrocarbon molecules are broken down into lighter molecules by means catalyst. As the thermal cracking process employed in the breakdown of the larger distillates molecules simply by the application of heat become obsolete due to inadequate product quality control and relatively poor engine performances of gasoline product, catalytic cracking became a better replacement.

This is the widely used process in refinery industry and serves to amend the disadvantages observed in thermal cracking.

The discovery of catalytic cracking process stemmed its root from work carried out by Eugene Houdry in the 1920s that better yield quality gasoline could be produced by treating heavy distillates at high temperatures with acidified montillonites clays. This led to the introduction of catalytic in 1936. Some few years after the technique was

developed into what is certainly the most important fluidized bed process, and probably the most important catalytic process in all industries. However, one of the central problems encountered in catalytic cracking is the rapid deactivation of catalyst caused by the surface deposition of a solid hydrocarbon polymer of high molecular known as coke. This ill-defined deactivation is due to the formation of catalyst surface. The catalyst is however regenerated by burning off coke deposit with air.

The first large scale catalytic cracking process, the Houdry process, used several fixed bed reactor connected in parallel so that continuous operations could be maintained while individual beds were undergoing a sequence of reaction, purging, regeneration and further purging. The setbacks of this intermittent mode of operation are obvious, and it was in an attempt to overcome them, and of the gasoline product, that first the moving bed and then the fluidized bed catalytic cracking (FCC) process were developed. The first FCC plant started operation at the Baton Rouge refinery of the standard oil company in 1942.

2.3 FLUIDIZED CATALYTIC CRACKING

Fluid catalytic cracking (FCC) is refinery process meant for increasing the ratio of light to heavy product from crude oil. Its objective is to crack high molecular weight hydrocarbon so to give a good yield of gasoline.

Though, the FCC process is highly complex, it is still flexible and can accommodate a wide range of feedstock from straight run distillates to heavy cycle oil. Its mechanism is complicated from both hydrodynamic and chemical point of view.

It is more common however for FCC feedstock's to be taken from vacuum distillation unit as a material containing low concentrations of catalyst fouling agents such metal (Ni and V), heavy asphaltines and heterocyclic compound.

Years after the invention of first FCC plant in 1942, there were improvements in engineering design, most of which were aimed at reducing both the size of the reactor units and the amount ancillary equipment required. Despite the considerable variation in reactor configuration that developed during this period the general principle in all designs is the same.

Cracking is carried out in one vessel where the hot catalyst is fluidized with vaporized feed. Deactivated catalyst flows from the reactor through either a standpoint or a riser to the regenerator where it is fluidized with air and the deposit is burned off.

2.4 FLUIDIZATION

Fluidization refers to those gas-solids and liquids solid system in which the solids phase is subjected to behave more or less like a fluid by the upwelling current of gas or liquid stream moving through the bed of solid particles. Thus even when the bed is accommodating strongly exothermic or endothermic process, it is normally completely isothermal with the solids particles being mixed very well. In this vein owing to their liquid- like properties, fluid- beds are capable of being transferred mechanically from one container to another thereby facilitating the handling of solids which need to be subjected to different physical or chemical operation in different vessel.

Cracking of heavy crude oil fractions of petroleum and fluidized bed combustion are good examples of fluidization.

The two basic types of fluidization are ;

- Particulate fluidization.
- Aggregative or bubbling (gas-solids) fluidization

2.4.1 ADVANTAGES OF FLUIDIZATION.

The chief advantages of fluidization are as follows

- The solids is vigorous agitated by the fluid passing through the bed.
- The mixing of the solid ensures that there are practically no temperature gradients in the bed even with quite exothermic or endothermic reactions.
- The fluid- beds are capable of being pumped from one container to another thereby facilitating the handing of solid which needs to be subjected to different physical or chemical operation in different vessels.

2.4.2 DISADVANTAGES OF FLUIDIZATION

The main disadvantages of fluidization are;

- Uneven contacting of gas and solid.
- Erosion of vessel internal and attrition of solid. Cont

2.4.3 GAS- SOLID FLUIDIZATION

Beds of solids fluidized with air (gas) usually exhibit what is called aggregative or bubbling (gas-solid) fluidization. Its application dominates the fluidization field .

Fluidization – a bed of solid particle with a gas provides the means of bringing the two into intimate contact and this can be very useful in an industrial context where large quantities of solids material have to be processed. The basic concepts of a gas – fluidized bed are illustrated in fig 2.4.3.

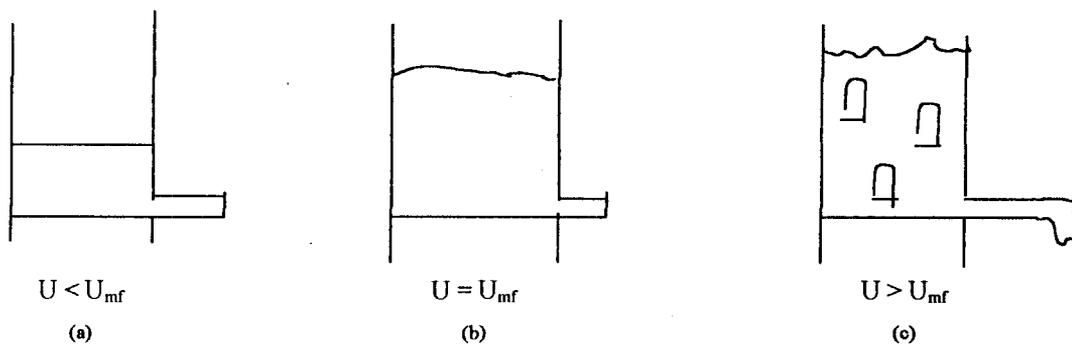


Fig 2.4.3 fluidized bed behaviour where U is the superficial gas velocity and U_{mf} is the minimum fluidization velocity (a) Packed bed, no flow; (b) fluid bed, uniform expansion; and (c) bubbling fluid bed, flow.

Gas velocity in fluidization beds is normally expressed as a superficial velocity, U ; the gas velocity through vessels assuming the vessel is empty. At a low gas velocity, the solids do not move. This constitutes a packed bed. As the gas velocity is increased the pressure drop increases until the drag plus the buoyancy forces on the particle overcome its weight and interparticle forces. At this point, the bed is said to be minimally fluidized and this gas velocity is termed the minimum fluidization velocity, U_{mf} . The bed expands slightly at this condition and the particles are free to move about. As the velocity is increased further, bubbles can form. The solid movement is more turbulent and the bed expands to accommodate the volume of the bubbles.

A bed of cracking catalyst of about 60 microns average particle size is fluidized at upward gas velocity of 60 - 100 cm/s and in almost all respect acts like a fluid with density of $0.40 - 0.65\text{gm/cm}^3$. Hence by selection of high velocity, catalyst can also be made to flow through pipes in an upward direction.

2.4.4 TERMS USED IN GAS – SOLID FLUIDIZATION

2.4.4.1 MINIMUM FLUIDIZATION VELOCITY, U_{mf}

This is the superficial velocity at which the drag forces plus the buoyancy force acting on the particle within the container is just equal to its gravitational force and any inter particle force holding the particles. It is the velocity required to just fluidize a bed of solid. Its value depends on the physical properties of the gas and of the solid particles. It is found by measuring the pressure drop across the bed as a function of gas velocity.

A number of empirical expressions are available which give the value of U_{mf} for a particular powder in terms of the physical properties of the solid particle and of the fluidizing gas. One of such empirical expression is the Zenz plot.

On the assumption that a bed of particles could be considered equivalent to an assembly of parallel cylindrical channel with internal surface and volume equal to the particle surface and the pore volume respectively. Kozeny(8) derived an expression using Hagen – Poiseuille equation for laminar flow through cylindrical tube of diameter d .

$$U = (d^2/32\mu) \times (\Delta p/h) \quad (1.1)$$

Where U is the velocity of the gas moving in laminar flow through a bed of porous material of depth h .

Below expression is obtained

$$U = (\epsilon^3/k\mu s^2) \times (\Delta p/h) \quad (1.2)$$

Where ϵ is the bed void fraction. μ is the fluid viscosity. S is the particle surface area per unit volume of the bed and k is a constant. For spherical particle of diameter d_p ,

$$S = 6(1-\epsilon)/d_p \quad (1.3)$$

By substituting for s in equation 1.2

$$U = (\epsilon^3 / (1-\epsilon)^2) \times (d_p^2 / 36k\mu) \times (\Delta p/h) \quad (1.4)$$

On the basis of experimental evidence Carman proposed a value for k of 5.0 thus enabling equation 1.4 to be written as

$$U = (\epsilon^3 / 180(1-\epsilon)^2) \times (d_p^2 / \mu) \times (\Delta p/h) \quad (1.5)$$

This equation is known as Carman – Kozeny (8) equation and it is applicable to a wide range of condition in which fluid flow through porous solid.

For bed of non – spherical particle, it is necessary to introduce a sphericity factor ϕ which is equivalent to the ratio of the surface area of the sphere of volume equal to that particle to surface area of particle.

Thus $\phi = 1$ for perfect spheres and $0 < \phi < 1$ for other shapes. The sphericity of most FCC catalyst are usually 0.99.

The Carman – Kozeny (8) is employed to obtain an expression for particle pressure drop through a vertical bed of height, H_{mf}

$$\Delta p / H_{mf} = (180(1-\epsilon)^2 / \epsilon^3) \times (\mu U / (\phi d_p)^2) \quad (1.6)$$

The minimum fluidization velocity is found to be

$$U_{mf} = \epsilon_{mf}^3 / 180(1 - \epsilon_{mf}) \times ((\rho_s - \rho_g) (\phi d_p) g) / (\phi d_p)^2 \quad (1.7)$$

ρ_s and ρ_g are densities of particles and gas respectively.

However with beds of particles greater than about 150 μ m in diameter inertial force become important and it is then necessary to use the Ergun equation⁸ in the determination of U_{mf} .

$$\Delta p/h = (150(1-\epsilon)^2 / \epsilon^3) \times (\mu U / (\phi d_p)^2) + (1.75(1-\epsilon) / \epsilon^3) \times (\rho_g U^2 / (\phi d_p))$$

2.4.4.2 MINIMUM BUBBLING VELOCITY U_{mb}

This is the velocity reached as the gas velocity is increased above U_{mf} . At this velocity it is observed experimentally for many powders that gas bubbles form within the bed and rise to the surface where they burst in the same way as gas bubbles in a boiling vessel.

At this velocity, the bed is divided essentially into two phases – The dense or emulsion phase where gas percolates through, as in packed bed and the lean or bubble phase where much of the gas is out of contact with solids.

Bubbles are formed in fluidized – beds from the inherent instability of the two phase systems. They are formed for group A powder (e.g. Zeolites) where the gas velocity is sufficient to start breaking interparticle forces. Bubbles or gas void exist in most fluidized bed and their role can be important because of the impact on the rate of exchange of mass and energy between the gas and solids in the bed. Bubble size control is achieved by controlling particle size distribution, and in particular the < 44mm fines fraction. About 25% fines are optimal for minimal bubble size, and hence for best conversion and highest heat transfer. Industrial processes are normally operated under condition with suppress bubble formation and growth. Small bubble size improves heat transfer and conversion.

2.4.4.3 TERMINAL VELOCITY U_t

The single – particle terminal velocity, U_t is the gas velocity required to maintain a single particle suspended in an upwardly flowing gas stream. Knowledge of terminal velocity is important in fluidized beds because it relates to how long particles are retained

in the system. If the operating superficial velocity on the bed fluidized bed far exceeds the terminal velocity of the bed particles, the particles are quickly removed.

Equations 1 to 4 indicate the method by which terminal velocity may be calculated from a hydrodynamic force balance that considers gravity, buoyancy, and drag but neglects inter particle force, the single terminal velocity is

$$U_t = [(4g d_p (\rho_p - \rho_g)) / (3 \rho_g C_d)]^{1/2}$$

Assuming spherical particles, the drag coefficient C_d , in the laminar, the Stokes flow regime is

$C_d = 24/R_{ep}$ where the particle Reynolds number, R_{ep} is defined as

$$R_{ep} = d_p \mu \rho_g / \mu$$

Where μ is the fluid velocity. The single spherical particle terminal velocity is then

$$U_t = [(g (\rho_p - \rho_g) d_p^2) / 18 \mu] \quad \text{for } R_{ep} < 0.4 \text{ for large properties, } C_d \text{ is } 0.43 \text{ and}$$

$$U_t = [(3.1 (\rho_p - \rho_g) g d_p) / \rho_g]^{1/2} \text{ for } R_{ep} > 500$$

This equation indicates that for small particles, viscosity is the dominant gas property and that for large particle density is more important. Both equation neglect interparticle forces.

2.4.4.4 PARTICLE REGIMES

This encompasses the classification of particle with respect to how they fluidize in air at ambient condition into Geldart group. Under these classifications we have up to about four groups: They are gouge A group B group C and Group D.

Group A particles are characterized by relatively small particle size ($d_p = 30$ to $150 \mu\text{m}$) and a low particle density (less than 1500Kg/m^3). Frequently these particles show an increase in the void fraction of the emulsion phase as the fluidizing gas velocity

increases. The minimum bubbling velocity, U_{mb} is always greater than U_{mf} Group A particles have the ability of holding aeration and feature explains why they flow well in transfer pipes in and out of the fluidized bed. Most manufactured fluid cracking catalyst eg Zeolites a typical example of a group A particles

Group B particles are dense particles which glass, sand and ore. The gas velocity at which bubbles first appear in the bed is $U_{mb}=U_{mf}$. Group B particles typically have an average particle size from 100-700 μ m.

Group C are usually less than 30 μ m in average particle diameter and smaller and lighter than group A particle. Group Particles are large .on the order of 1 or more millimeter (1000 μ m) in average particle size. In a fluidized bed, they behave similarly to group B particle.

The table below shows the classification of some particles into Geldart group and their particulate properties, (8)

Geldart Group	particle	Average Particle size Dp, Um	Particle Density ρ_p , kg/m ³	Angle of Internal friction. deg	Angle of Repose deg	Sphericity Ψ
A	FCC Catalyst	60	1400	79	32	0.99
B	Sand	500	2000	64	36	0.92
C	Ion exchange resin	30	800	82	29	0.86
D	TCC beads	3000	1000	72	35	1.0

2.5 CATALYST

Catalysts are widely used to accelerate the rate of chemical reactions. In catalyzed reactions, the basic laws of chemistry and thermodynamics are observed, but the presence of catalyst greatly influences the chemical reaction.

In making, the first catalysts that were employed industrially were naturally-occurring clays such as montmorillonite. These were gradually superseded by synthetic clays-the amorphous silica-alumina which in turn has been largely replaced by the synthetic crystalline Zeolites. The latter account for over 90% of all cracking catalysts currently in use.

The natural clays have two main disadvantages in use. They are deactivated rather too readily by sulphur compounds and are sensitive to high regeneration temperature. due to these. Improvements were made. Resulting into the generation of superior synthetic-silica aluminas. It was the technological improvement of the latter that brought the use of crystalline synthetic zeolite.

2.5.1 ZEOLITES

The Zeolites are porous, crystalline alumina silicates many of which have the general formula $M_{x/n} [(AlO_2)_x(SiO_2)_y].ZH_2O$ where x/n is the number of exchangeable cations, M, of valency n. about forty different types of zeolite are known to occur naturally but only one, the rare mineral faujasite, is relevant to catalytic cracking. The basic unit of the faujasite structure is the cubo-octahedron made up of twenty four tetrahedral of either SiO_4^{4-} or AlO_4^{5-} . These are connected through their hexagonal faces to give an assembly of 192 tetrahedral in a large cubic unit cell with an edge of $24.95^{\circ}A$.

Zeolites have good number of space. They are excellent absorbent because of their poor size. This varies from 0.3-1.3nm. They have screening properties i.e. can pass through the space of a crystal and absorb only molecules of a definite size not larger than their pore diameter.

A feature of catalytic cracking catalyst is their rapid deactivation. The catalyst pores become clogged with coke after ten to fifteen minutes of operation. Therefore, Cracking constantly has to be altered with catalyst regeneration.

2.5.1.1 ADVANTAGES OF ZEOLITE CATALYST.

- i. Higher gasoline yield at a given conversion
- ii. Increases isobutene production
- iii. Higher activity
- iv. Lower coke yield
- v. Ability to higher conversion per pass without over cracking.

2.5.2 PARAFFIN CRACKING

Cracking reactions involve the rupture of C-C bonds, and since they are endothermic reactions. They are thermodynamically favoured by high temperature.

Paraffin is cracked to give olefins and smaller paraffins.

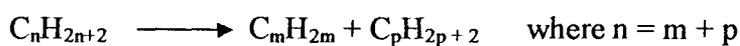
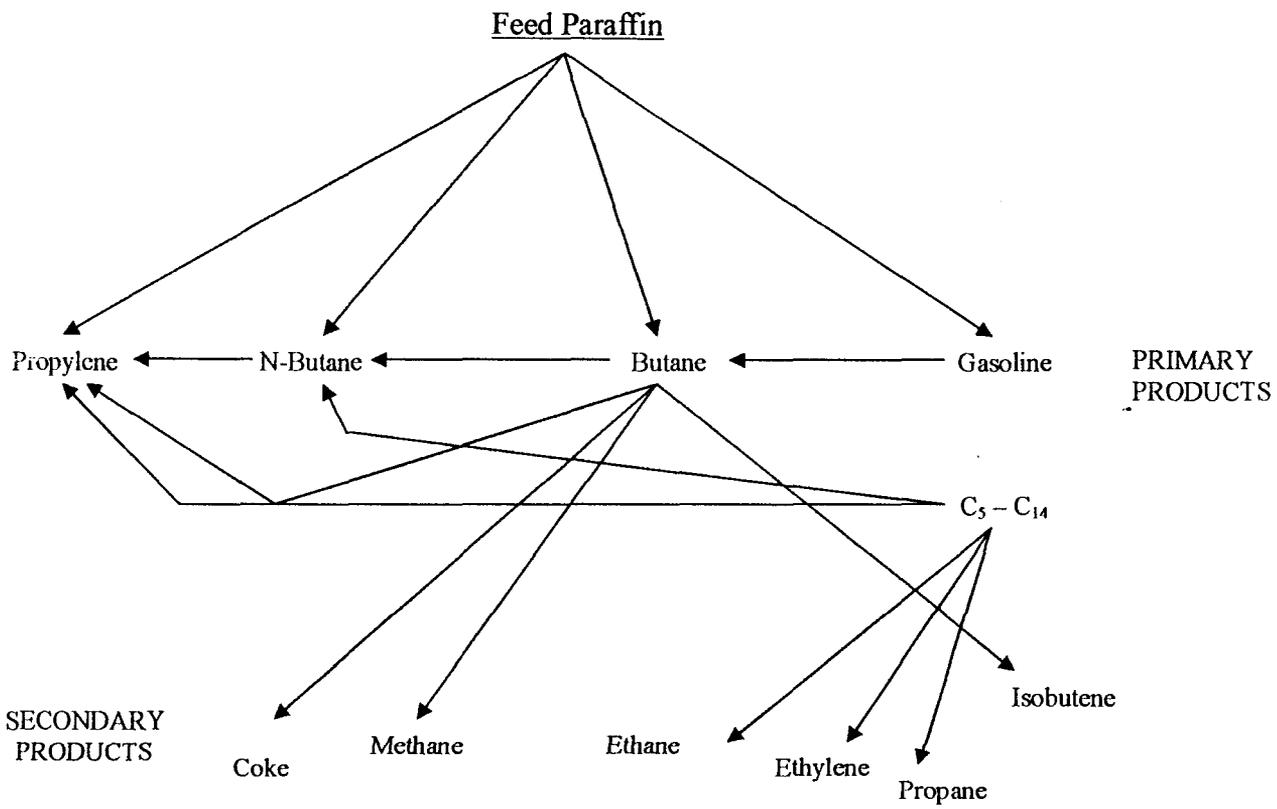
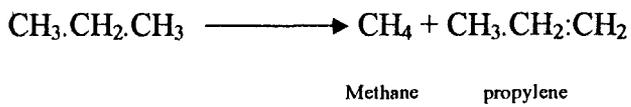


Fig 2.5.2 A detailed reaction scheme for catalytic cracking of paraffins is given below.



2.5.2.1 MECHANISM FOR CRACKING BUTANE

From the experimental work of Hurd and Spence (11) on the decomposition of n-butane at 600°C (1112°F).



And



At 600°C, the first of these appears to proceed to the extent of about 55% and the second to 40%. Dehydrogenation reaction into butane and butadiene appears to represent less than 5% of the total.

The extent to which each of the reaction takes place depends upon the temperature and the pressure. Low-pressure operations have been explored but butanes are also cracked at high pressure especially of the recovery of butylenes is desirable.

The reaction for the cracking of butane using zeolite acidic site catalysts $(\text{Na}_{56} \text{Al}_{56} \text{Si}_{136} \text{O}_{384} 250 \text{H}_2\text{O})$ i.e. zeolite acidic site Y-Zeolites or $\text{Na}_{56} [(\text{AlO}_2)_{56} (\text{SiO}_2)_{136}] 250 \text{H}_2\text{O}$.

The products include H_2O , paraffin and olefins. The result demonstrates the relevance of super acid solution chemistry to catalysts by a solid acid at a much higher temperature.

2.5.2.2 RATE OF CRACKING

The yield in a given length of time increases rapidly with temperature, the yield at a fixed temperature increases with time up to a certain point and then decreases, and the yield for a given length of time is greater for heavy stocks. Then the lighter the cracking stock, the larger the time required.

In general, stocks that require a relative long time for a given yield are termed refracting stocks. Recycle stocks, kerosene, naphtha, and gasoline are classed as refractory stock.

The cracking reaction is of first order reaction of the decomposition is limited as in conventional cracking operations to a low conversion per pass (20-25%)

$$K_1 = \frac{1}{t} \ln \frac{100}{100 - x}$$

Or often

$$K_1 = \frac{1}{t} \ln \frac{a}{a - x}$$

Where K_1 = reaction velocity constant

t = time (sec)

a = percentage of materials in feed stock, for a

pure feed stock $a = 100\%$

x = percentage of material that disappears during the reaction

the reaction time, t

For hydrocarbons (ethane from heptane), the term x is used as mole (or gas volume) percentage and it refers to the disappearance of the feed stock hydrocarbon.

2.5.5.3 COKE FORMATION

The coke burned in an FCCU regeneration is a purely defined hydrocarbons material that has either not been desorbed from the catalyst surface or has not been purged from between catalyst particles during the passage of the catalyst through the steam stripper. This coke originates from four different sources

- i. Catalytic coke is produced directly from the acid catalyzed cracking reaction.
- ii. Contaminant coke arises from the dehydrogenation activity of contaminating metals (principally nickel and vanadium) in the feed to the FCCU.
- iii. Additive coke is directly related to high boiling, refractory components in the feed to the FCCU.

- iv. Cat –to- oil coke is related to the catalyst circulation rate and derives from the hydrocarbons leaving the stripper.

The amount of catalytic coke formed during catalytic cracking depends on the type of catalyst used in the FCCU, the coking tendency of the feed, the degree of conversion of the feed, and the length of time the catalyst is exposed to the feed.

$$\text{Coke on catalyst} = Kt^{0.5}$$

Coke deposition is essentially independent of space velocity. These observations, which were developed from the study of amorphous catalysts during the early days of catalytic cracking, still, characterize the coking of modern day FCC catalysts over a wide range of hydrogen – transfer (H- transfer) capabilities.

Coke in a spent catalyst is often referred to as delta coke (DC), the coke content of the spent catalyst the coke content of the regenerated catalyst.

2.6 PROCESS VARIABLE AND OPTIMIZATION

2.6.1 PROCESS VARIABLE

In addition to the nature of the charge stock, the major operating variable affecting the conversion and product distribution are the cracking temperature, catalyst, space velocity and activity and recycle ration. For better understanding of the process, several terms should be defined.

CONVERSION: $100 \frac{\text{volume of feed} - \text{volume of cycle stock}}{\text{Volume of feed}}$

SELECTIVITY: The ratio of yield of desirable products to the yield of undesirable product to the yield of coke and gas.

YIELD: This is ratio of the quantity of product actually obtained to its maximally obtainable quantity.

CATALYST TO OIL RATIO: Is the Kg per hr of catalyst divided by the Kg per hr of raw oil charge.

EFFICIENCY: $\frac{\% \text{ gasoline}}{\% \text{ conversion}}$

ACTIVITY: Ability to crack a gas to lower boiling fraction.

High conversion is due to increasing temperature, but decreasing yield of gasoline, due to secondary cracking to smaller products:

TEMPERATURE: 520-550⁰C

PRESSURE: 2-3 atm

CAT/OIL: 4.5-6

CONTACT TIME: 2-6 secs.

CONVERSION: 70-80%

2.6.2 PROCESS OPTIMIZATION

The fluid catalyst cracking unit (FCCU) is one of the most important units in the refinery. Few FCCU have real time process optimization implemented since feeds typically have been measurable only in the laboratory. These measurements take many hours with reports available only once or twice a day. Even the measurement of PIONA (paraffins, isoparaffins, olefins, naphthenes, and aromatics) and the distillation properties of the rundowns are difficult to achieve on line.

FCCU controls and optimization include feed preparations, the reactor/regenerator, the main fractionator, the wet gas compressors maximizing yield of most valuable product, optimization energy utilization, controlling conversion and downstream gas plant.

Catalytic cracking is an endothermic reaction hence, the equilibrium conversion for the catalytic cracking of butane increases with increasing temperature.

The optimum operating temperature can be determined from the curve of conversion (extent of reaction), X against temperature, T or be calculated from the value obtained from the equilibrium temperature.

$$T_{op} = T_{eq} / [1 + 2.3RT_{eq}/mg \log (E+mg/E)]$$

Where T_{op} = optimum temperature

T_{eq} = equilibrium temperature.

R = gas constant (8.31KJ/mol.K)

m = coefficient. It is the stoichiometry of the of the major component when 1M of the desired product is produced.

q = heat of reaction

E = activation energy, KJ/mol

Optimum operating temperature depends on the nature and concentration of the reactants, extent of conversion of raw materials to the final products, contact surface area and in some case the activeness of the catalyst.

2.6.3 KINETIC OF CRACKING

For a tubular reaction, the differential form of design equations

$$F_{AO} dx/dv = -r_A$$

And the corresponding equation for a tubular reactor that has fluid-solid or catalytic occurring in it is.

$$F_{AO} dx/dw = -r_A$$

The reaction rate is based on mass of solid, W rather than in reactor volume, V.

The mass of solid is used because the amount of catalyst or the amount of the solid reactant present is what is important to the rate of reaction. The reactor volume that contains the catalyst or other solid is of secondary significance.

For a first order reaction, that is

$$F_{AO} dx/dw = -r_A = KC_A$$

The plot of the graph of $F_{AO} dx/dw$ against C_A gives a straight line graph which passes through the origin. K is the slope and is taken as the rate constant

CHAPTER THREE

3.0 EXPERIMENTAL PROCEDURES

3.1 EXPERIMENTAL TECHNIQUES

TITLE: Determination of optimum conversion of catalytic cracking of butane in a fluidized bed reactor.

AIM/OBJECTIVE: To determine the optimum variable conditions and rate of reaction for the catalytic cracking of butane in a fluidized reactor.

APPARATUS/ EQUIPMENTS:

- Fluidized bed catalytic cracking prototype reactor
- Zeolites catalyst
- Electronic weighing machine
- Cylinder containing butane
- Measuring cylinder and bottle
- Flow rate meter
- Stop watch
- Adaptor
- Thermometer
- Petroleum ether.

3.2 DIAGRAM

- | | | | |
|---|-------------------|----|---------------------|
| 1 | Prototype F.C.C.R | 9 | thermometer |
| 2 | Cyclone | 10 | Retort stand |
| 3 | Zeolites catalyst | 11 | product chamber |
| 4 | Butane (feed) | 12 | fluidization region |
| 5 | Heat exchanger | | |
| 6 | Dust collector | | |
| 7 | Pressure gauge | | |
| 8 | Pipe | | |

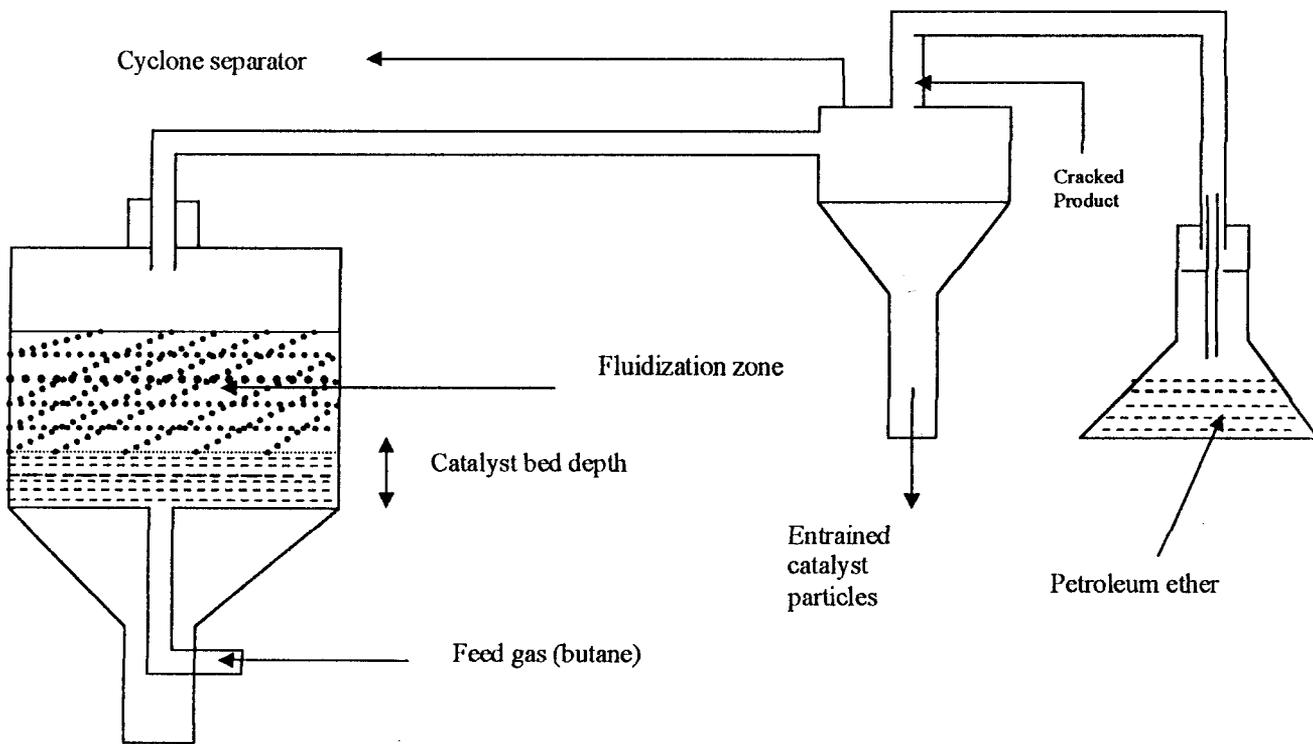


Fig 3.1 Sketch of a laboratory fluidized bed catalytic reactor.

3.3 METHODOLOGY

1. The catalytic cracking prototype reactor was clean and set in order.
2. The zeolites catalyst was sieved to remove dusts and catalyst above sieve diameter, and those of below 250 μ m (i.e. sieve diameter) was collected with a pan.
3. The diameter of the tube was measured with vernier caliper and recorded.
4. The height of the tube was measured and recorded
5. 50g of the zeolites was measured and recorded
6. The zeolites was then poured into the reactor, and allowed to maintain a uniform bed height after which it was measured.
7. The flow rate meter was opened and the bed was fluidized
8. The operating pressure was measured and recorded.
9. The bubbling bed was allowed to fluidize for five minutes after which the flow rate meter was switched off and readings were taken.
10. The temperature at the top and bottom of the bed was also measured and recorded.
11. The product mixture was collected in the petroleum ether placed in container labeled A..
12. The product in the ether was sealed and labeled after which it was analyzed with gas chromatograph
13. Methods 5 to 15 were repeated for different weight of Zeolites. (i.e. 60 to 70)
14. The results of the analyzed products were tabulated below.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 EXPERIMENTAL RESULTS

Below are some of the parameters taken into consideration while obtaining the result: he parameters are

$$C_{A0} = \frac{P_{A0}}{RT}$$

$$X_A = 1 - \frac{C_{AF}}{C_{A0}}$$

Molar rate = F_{A0} = Initial concentration x Flowrate

$$F_{A0} = C_{A0}V$$

TABLE 4.1 RESULTS OF EXPERIMENTAL RUN

TABLE 1

T_1 ms	Temp($^{\circ}$ C)	$C_{A,in}$ (mol m $^{-3}$)	$C_{A, out}$ (mol m $^{-3}$)	$X_{A, ave}$ (mol m $^{-3}$)	$X_{A, in}$	$X_{A,out}$	ΔX_A	$\frac{\Delta X_A}{W/F_{A0}}$
	42	0.0611	0.0247	0.0429	0.0542	0.6176	0.5630	0.0847
	45	0.0605	0.0244	0.0425	0.0635	0.6223	0.5588	0.0841
	49	0.0598	0.0241	0.0420	0.0743	0.6269	0.5526	0.0832
	54	0.0589	0.0238	0.0414	0.0883	0.6316	0.5434	0.0818
	58	0.0581	0.0235	0.0408	0.1006	0.6362	0.5356	0.0807

TABLE 2

T_2 ms	Temp($^{\circ}$ C)	$C_{A,in}$ (mol m $^{-3}$)	$C_{A, out}$ (mol m $^{-3}$)	$X_{A, ave}$ (mol m $^{-3}$)	$X_{A, in}$	$X_{A,out}$	ΔX_A	$\frac{\Delta X_A}{W/F_{A0}}$
	41	0.0689	0.0223	0.0456	0.0523	0.6933	0.6410	0.1164
	47	0.0677	0.0219	0.0448	0.0688	0.6988	0.6300	0.1144
	51	0.0668	0.0216	0.0442	0.0812	0.7029	0.6217	0.1129
	54	0.0662	0.0214	0.0438	0.0894	0.7056	0.6162	0.1119
	59	0.0652	0.0211	0.0432	0.1032	0.7098	0.6066	0.1102

TABLE 3

S ₁ R ₁ Runs	Temp(°C)	C _{A,in} (mol m ⁻³)	C _{A, out} (mol m ⁻³)	X _{A, ave} (mol m ⁻³)	X _{A, in}	X _{A,out}	ΔX _A	$\frac{\Delta X_A}{W/F_{A_0}}$
1	43	0.0761	0.0186	0.0474	0.0570	0.7695	0.7125	0.1478
2	47	0.0752	0.0752	0.0468	0.0682	0.7732	0.7050	0.1463
3	52	0.0740	0.0740	0.0461	0.0832	0.7757	0.6927	0.1437
4	55	0.0733	0.0733	0.0456	0.0917	0.7782	0.6865	0.1424
5	59	0.0725	0.0725	0.0451	0.1016	0.7807	0.6791	0.1409

TABLE 4

S ₂ R ₁ Runs	Temp(°C)	C _{A,in} (mol m ⁻³)	C _{A, out} (mol m ⁻³)	X _{A, ave} (mol m ⁻³)	X _{A, in}	X _{A,out}	ΔX _A	$\frac{\Delta X_A}{W/F_{A_0}}$
1	62	0.0574	0.0205	0.0390	0.1115	0.6827	0.5712	0.08856
2	66	0.0568	0.0202	0.0385	0.1207	0.6873	0.5666	0.08785
3	70	0.0561	0.0200	0.0381	0.1316	0.6904	0.5588	0.08664
4	74	0.0555	0.0198	0.0377	0.1409	0.6935	0.5526	0.08568
5	78	0.054	0.0195	0.0372	0.1517	0.6981	0.5464	0.08471

TABLE 5

S ₂ R ₂ Runs	Temp(°C)	C _{A,in} (mol m ⁻³)	C _{A, out} (mol m ⁻³)	X _{A, ave} (mol m ⁻³)	X _{A, in}	X _{A,out}	ΔX _A	$\frac{\Delta X_A}{W/F_{A_0}}$
1	62	0.0646	0.0152	0.0399	0.1114	0.7909	0.6795	0.1234
2	65	0.0641	0.0151	0.0396	0.1183	0.7923	0.6740	0.1224
3	89	0.0633	0.0149	0.0391	0.1293	0.7950	0.6657	0.1209
4	74	0.0624	0.0147	0.0386	0.1417	0.7978	0.6562	0.1192
5	79	0.0617	0.0145	0.0381	0.1513	0.8006	0.6493	0.1178

TABLE 6

S ₂ R ₁ Runs	Temp(°C)	C _{A,in} (mol m ⁻³)	C _{A, out} (mol m ⁻³)	X _{A, ave} (mol m ⁻³)	X _{A, in}	X _{A,out}	ΔX _A	$\frac{\Delta X_A}{W/F_{A_0}}$
1	62	0.0646	0.0152	0.0399	0.1114	0.7909	0.6795	0.1234
2	65	0.0641	0.0151	0.0396	0.1183	0.7923	0.6740	0.1224
3	89	0.0633	0.0149	0.0391	0.1293	0.7950	0.6657	0.1209
4	74	0.0624	0.0147	0.0386	0.1417	0.7978	0.6562	0.1192
5	79	0.0617	0.0145	0.0381	0.1513	0.8006	0.6493	0.1178

Figure 4.1a : Graph of rate of reaction $-r_A$ Vs Concentration, C_A for 1st reaction

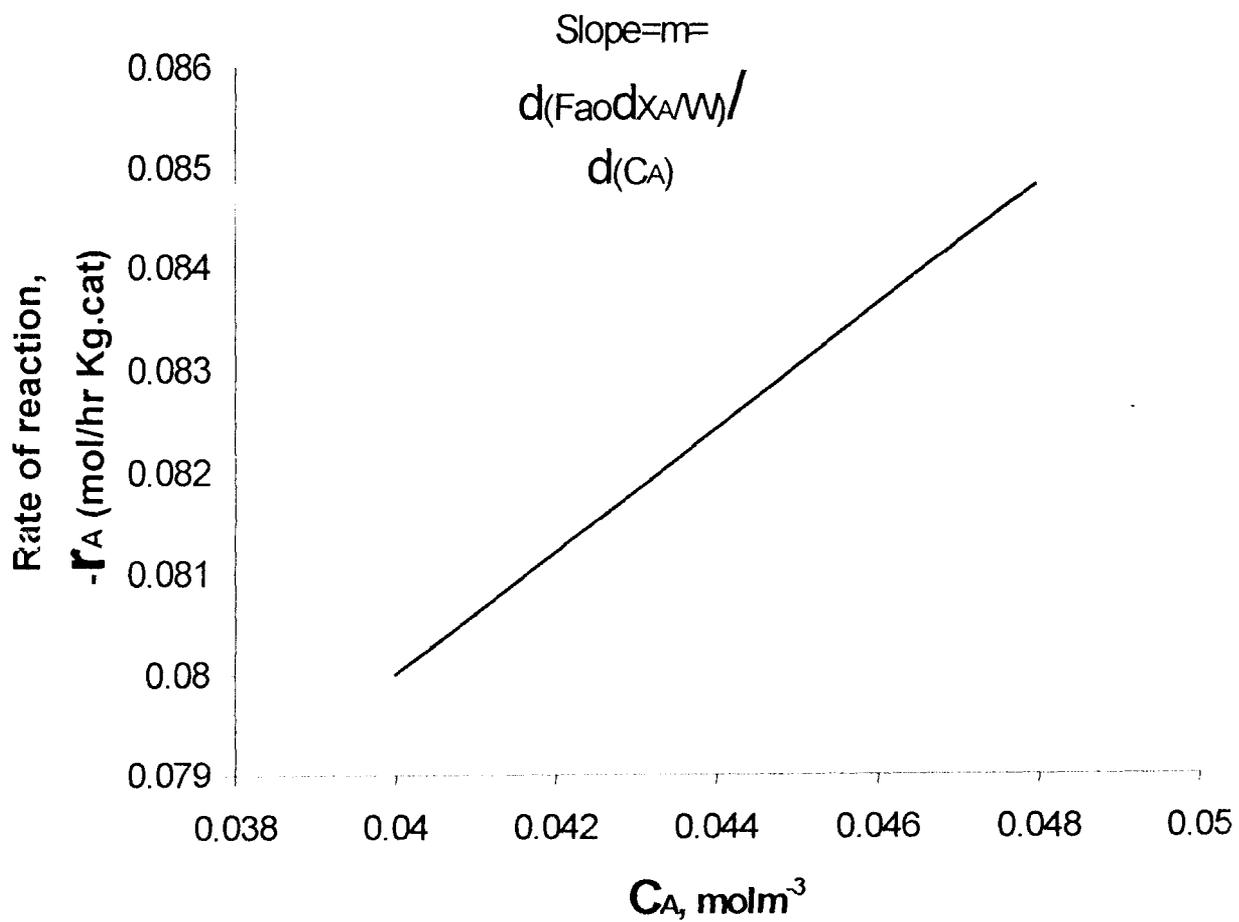


Figure 4.1b : Graph of rate of reaction $-r_A$ Vs Concentration, C_A for 2nd reaction

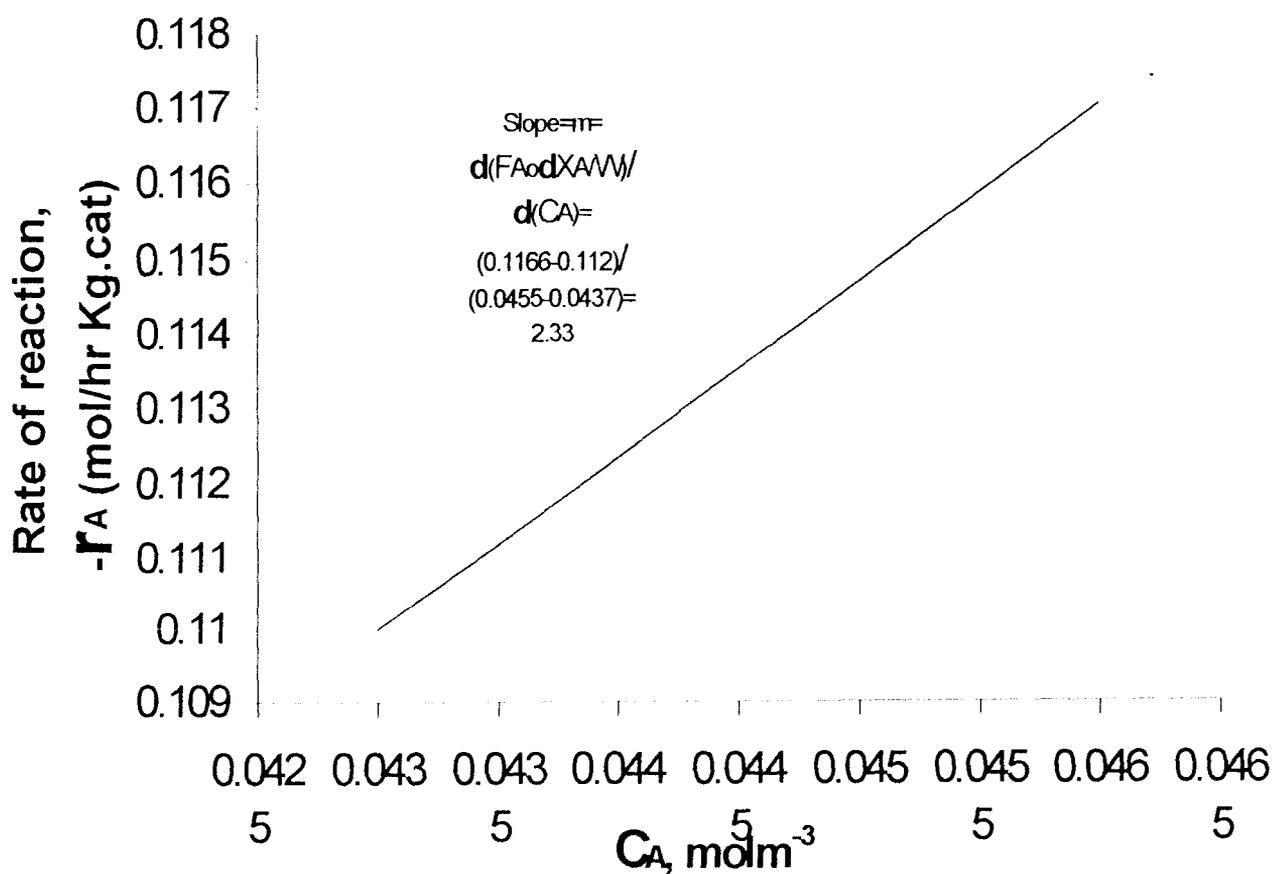


Figure 4.1c : Graph of rate of reaction $-r_A$ Vs Concentration, C_A for 3rd reaction

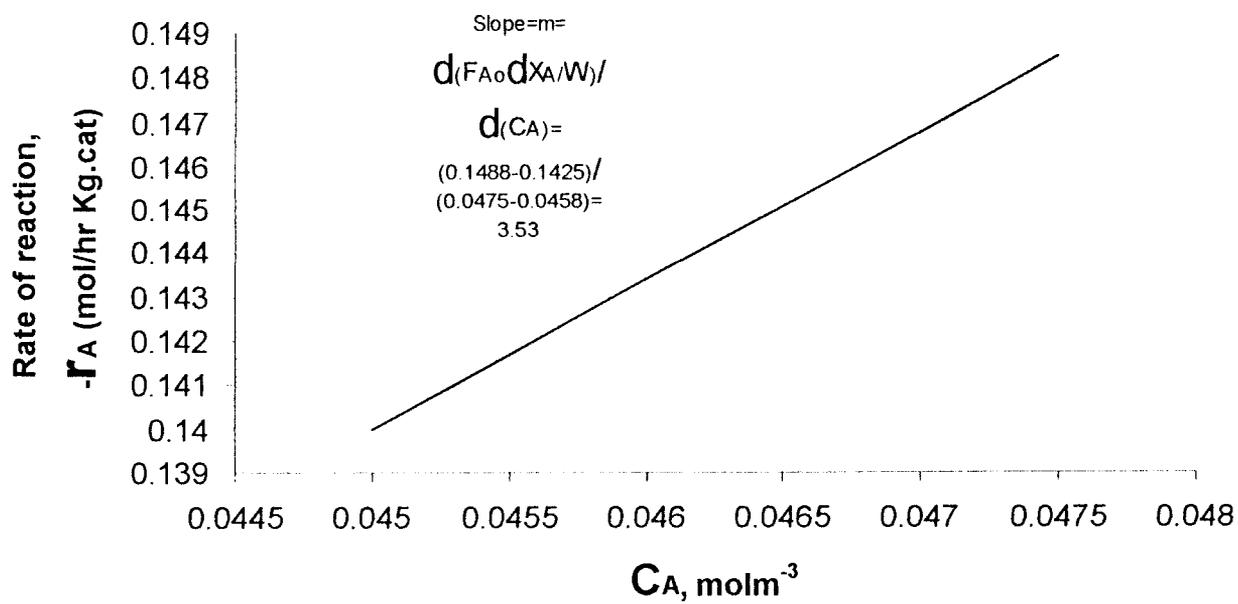


Figure 4.1d : Graph of rate of reaction $-r_A$ Vs Concentration, C_A for 4th reaction

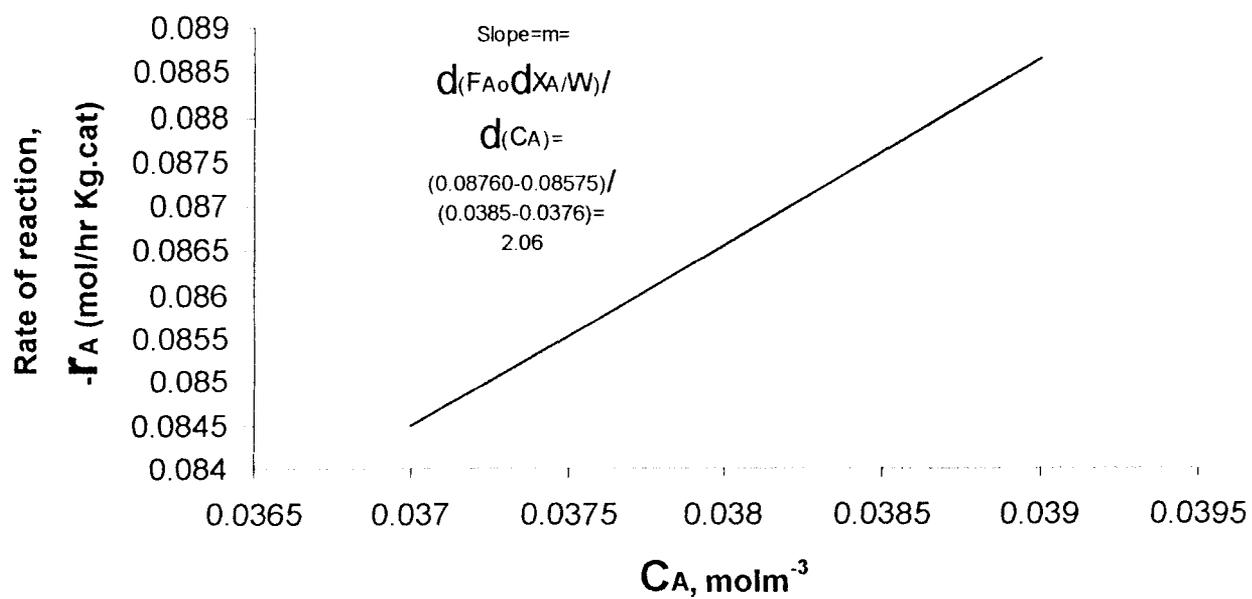


Figure 4.1e : Graph of rate of reaction $-r_A$ Vs Concentration, C_A for 5th reaction

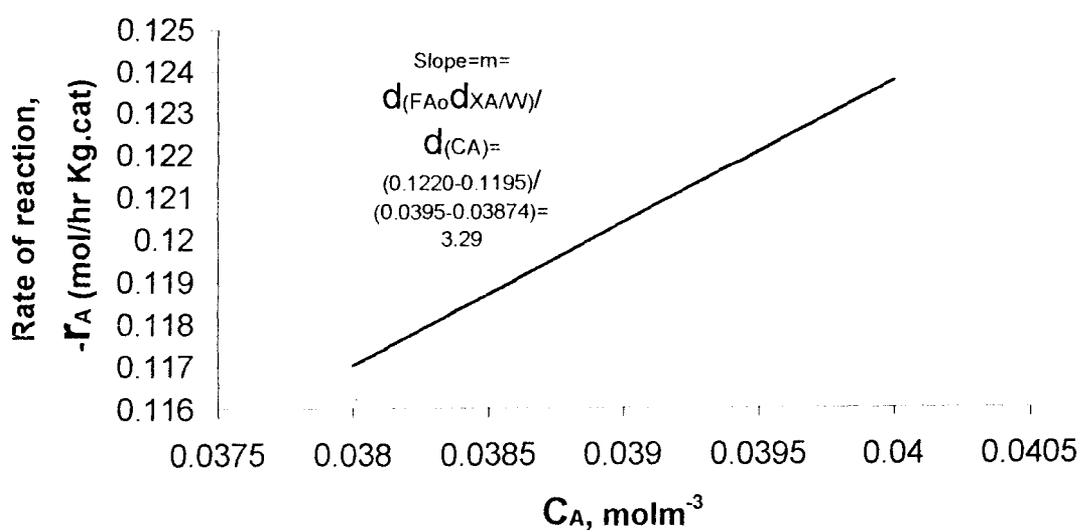


Figure 4.1e : Graph of rate of reaction $-r_A$ Vs Concentration, C_A for 5th reaction

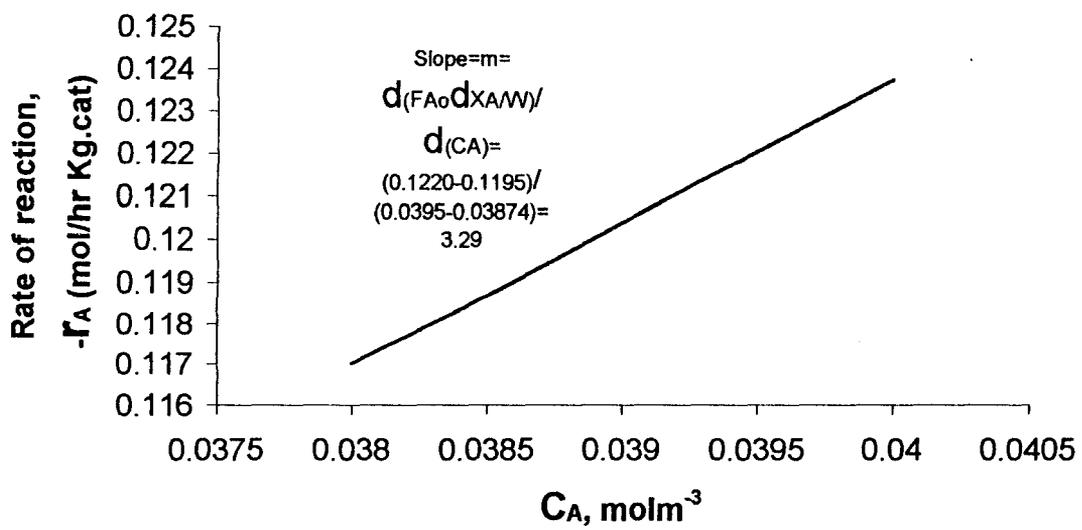
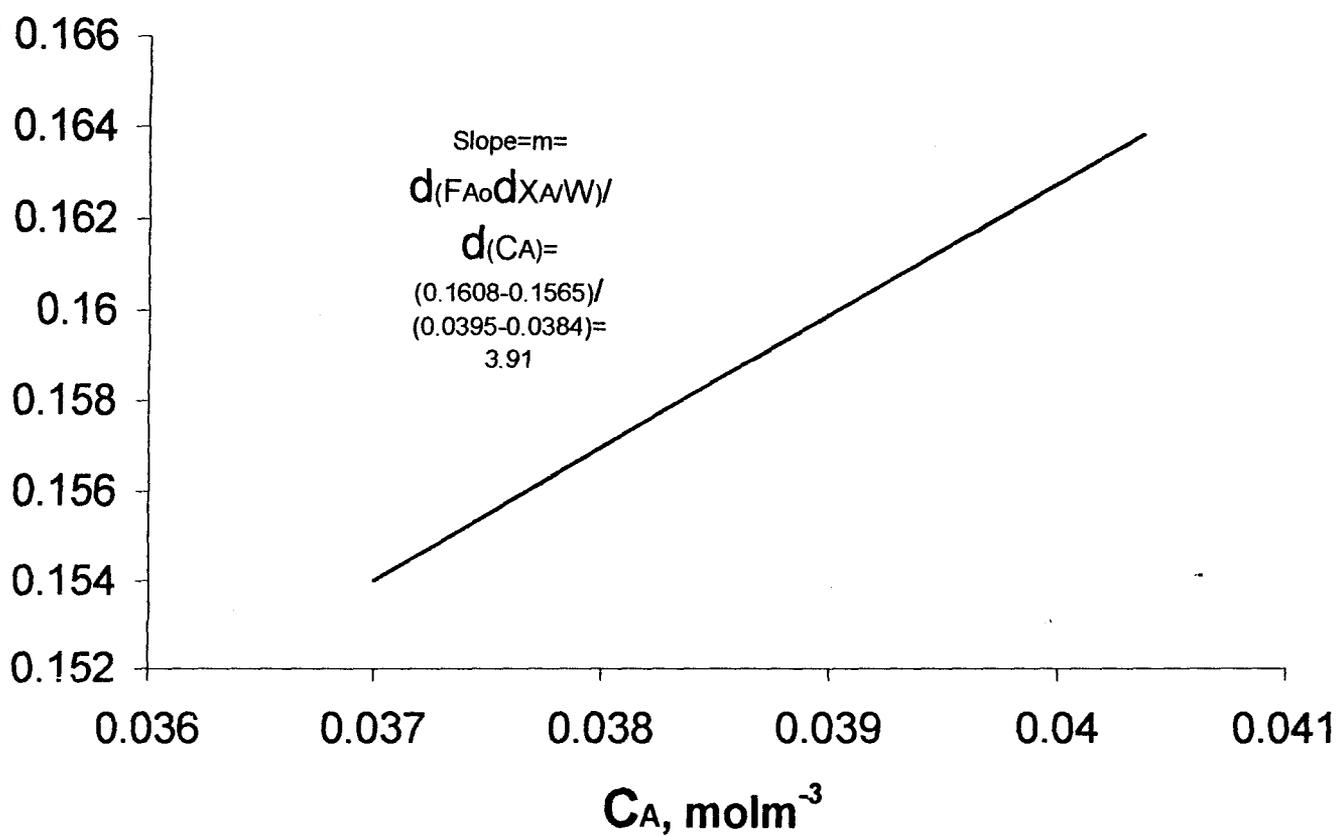


Figure 4.1f : Graph of rate of reaction $-r_A$ Vs Concentration, C_A for 6th reaction



ARRHENIUS PLOT(FIGURE 4.1g: Graph of $\ln K$ Vs Inverse of Temperature, $1/T$)

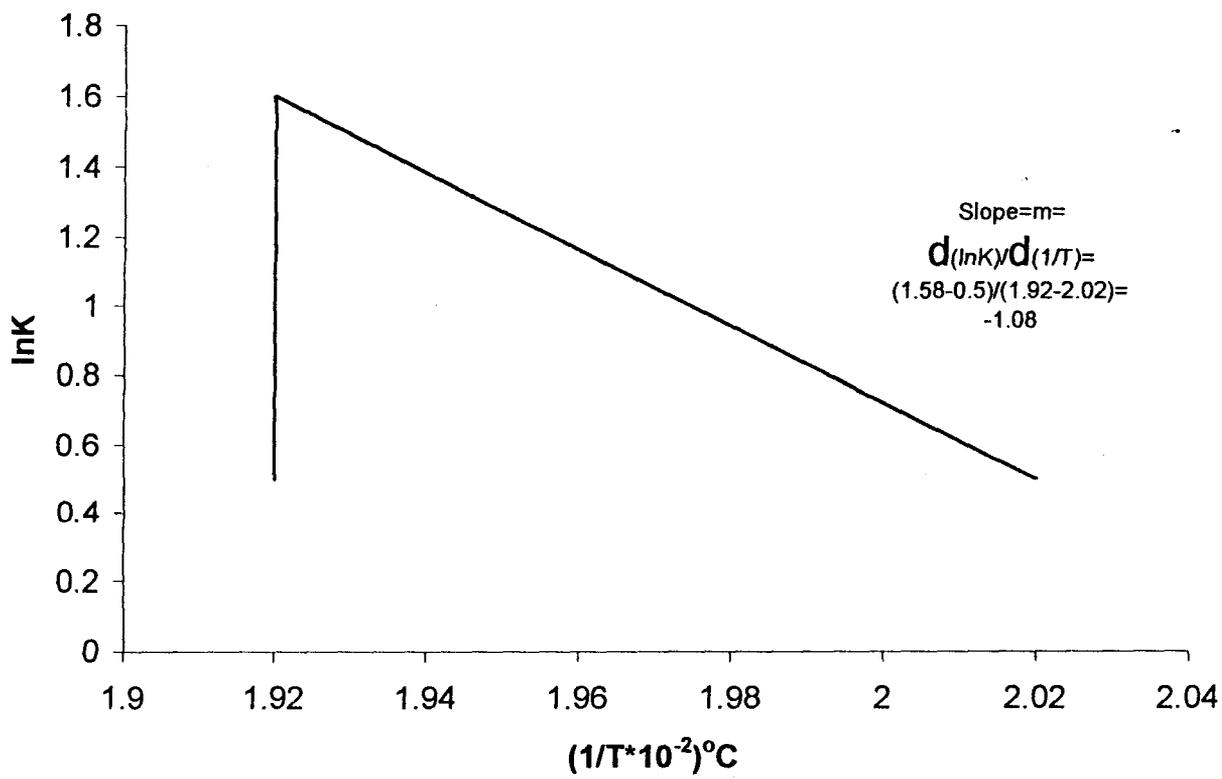
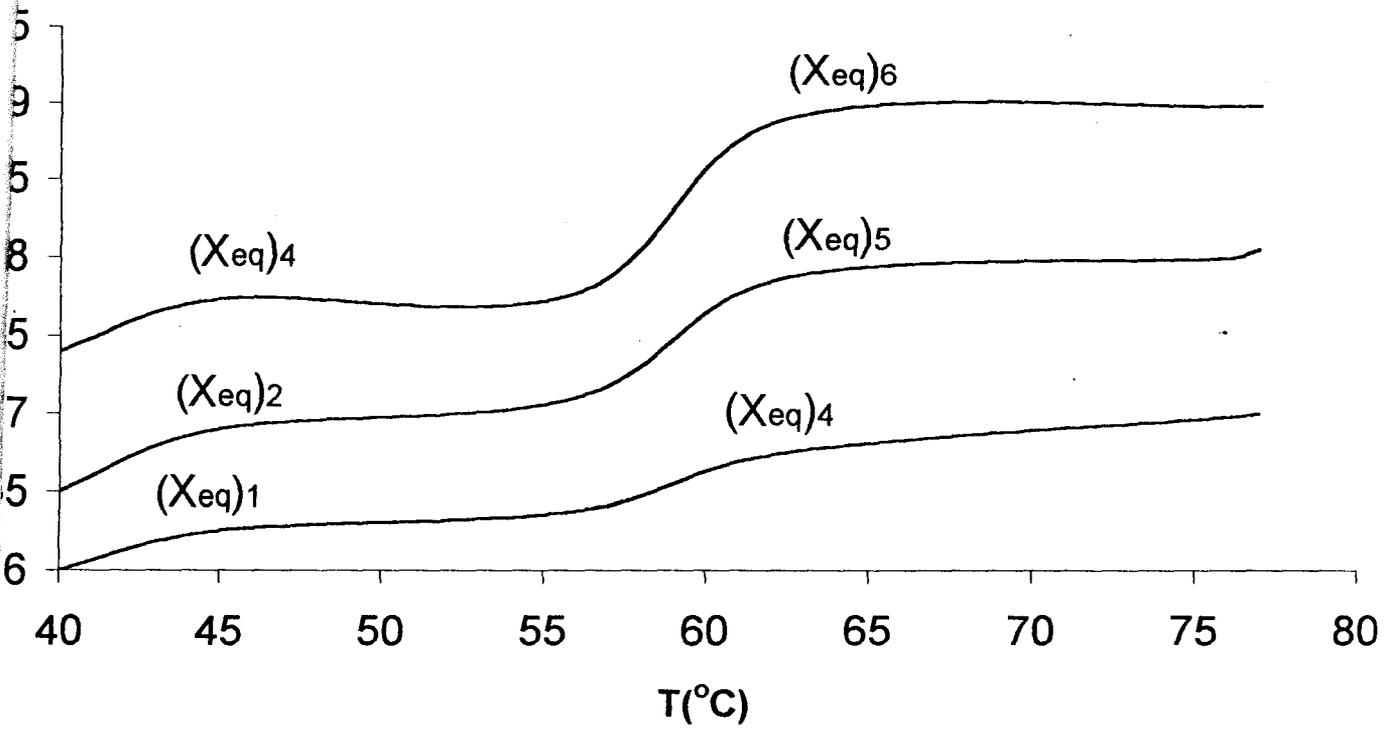


FIGURE 4.1h: Graph of conversion, X_A Vs Temperature,

T



4.2 CALCULATION

For a solid catalyst reaction the rate of reaction $-r_A = F_{A0} \frac{\Delta X}{\Delta W}$

Therefore from the result obtained from the experiment: by plotting the graph of

$\frac{\Delta X_A}{W/F_{A0}}$ Against C_A , a linear graph is obtained that passes through the origin.

Then the catalytic reaction is first order with the value of the slope as the rate constant. The values of K (i.e. the slope) for each run as follows

$$\begin{aligned} 1. \quad K_1 = \text{slope} &= \frac{\Delta(F_{A0} \frac{\Delta X_A}{W})}{\Delta(C_A)} = \frac{0.08405 - 0.08125}{0.0425 - 0.0408} \\ &= 1.65 \text{ mol/hr. kg cat} \end{aligned}$$

$$\begin{aligned} 2. \quad K_2 = \text{slope} &= \frac{\Delta(F_{A0} \frac{\Delta X_A}{W})}{\Delta(C_A)} = \frac{0.1162 - 0.0112}{0.0455 - 0.0437} \\ &= 2.33 \text{ mol/hr. kg cat} \end{aligned}$$

$$\begin{aligned} 3. \quad K_3 = \text{slope} &= \frac{\Delta(F_{A0} \frac{\Delta X_A}{W})}{\Delta(C_A)} = \frac{0.1485 - 0.1425}{0.0475 - 0.0458} \\ &= 3.53 \text{ mol/hr. kg cat} \end{aligned}$$

$$4. \quad K_4 = \text{slope} = \frac{\Delta(F_{A0} \frac{\Delta X_A}{W})}{\Delta(C_A)} = \frac{0.08760 - 0.08525}{0.0385 - 0.0376}$$

$$= 2.06$$

$$5. \quad K_5 = \text{slope} = \frac{\Delta(F_{A0} \frac{\Delta X_A}{W})}{\Delta(C_A)} = \frac{0.122 - 0.1195}{0.0395 - 0.03874}$$

$$= 3.29$$

$$6. \quad K_6 = \text{slope} = \frac{\Delta(F_{A0} \frac{\Delta X_A}{W})}{\Delta(C_A)} = \frac{0.1608 - 0.1565}{0.0395 - 0.0384}$$

$$= 3.91$$

An average temperature range was obtained for each run. The average temperature

each run are:-

$$1^{\text{st}} \text{ run, } T_{\text{ave}} = \frac{42 + 45 + 49 + 54 + 58}{5} = 49.6$$

$$2^{\text{nd}} \text{ run, } T_{\text{ave}} = \frac{41 + 47 + 51 + 54 + 59}{5} = 50.4$$

$$3^{\text{rd}} \text{ run, } T_{\text{ave}} = \frac{43 + 47 + 52 + 55 + 59}{5} = 51.2$$

$$4^{\text{th}} \text{ run, } T_{\text{ave}} = \frac{62 + 66 + 70 + 74 + 79}{5} = 69.8$$

$$6^{\text{th}} \text{ run, } T_{\text{ave}} = \frac{62 + 65 + 71 + 75 + 80}{5} = 70.6$$

From the Arrhenius equation i.e.

$$K = A_0 e^{-E/RT}$$

$$\ln K = \ln A_0 - \frac{E}{RT_{\text{ave}}}$$

From the result obtained so far the graph of $\ln K$ was plotted against $1/T_{\text{ave}}$. For each run. A straight line graph was obtained.

The expression $-E/R$ is the slope for the runs within the temperature range of 41 – 60 (i.e the 1st, 2nd, and 3rd runs)

$$\text{The slope} = \frac{-E}{R} = \frac{1.58 - 0.5}{1.92 - 2.02} = -10.8$$

$$-E/R = -10.8$$

$$E = 10.8 R$$

Where R is the gas constant = 8.314 KJ/mole

$$E = 10.8 \times 8.314$$

$$= 89.8 \text{ Kcal/gmole}$$

The graph of conversion, X_{Aout} was plotted against temperature, to determine the equilibrium and optimum conversion and temperature.

The following were deduced from the graph.

- At 0.05kg weight of catalyst, gas flow rate $0.12\text{m}^3/\text{hr}$ and gas pressure of 1.6 bar.

The equilibrium conversion, $X_{eq} = 0.62$

The corresponding equilibrium temperature $T_{eq} = 43^\circ\text{C}$

- At 0.06kg weight of catalyst, gas flow rate of $0.15\text{m}^3/\text{hr}$ and gas pressure of 1.8 bar

The equilibrium conversion $X_{eq} = 0.68$

The temperature equilibrium temperature = 44°C

- At 0.07kg weight of catalyst, gas flow rate of $0.18\text{m}^3/\text{hr}$, and gas pressure of 2.0 bar

The equilibrium conversion, $X_{eq} = 0.77$

The corresponding equilibrium temperature = 44°C

At an increased temperature i.e. (from $40 - 60^\circ\text{C}$)

At 0.05kg weight of catalyst, gas flow rate of $0.12\text{m}^3/\text{hr}$, and gas pressure of 1.6 bar

The equilibrium conversion, $X_{eq} = 0.685$

The corresponding equilibrium temperature = 62°C

At 0.06kg weight of catalyst, gas flow rate of 0.15m^3 , and gas pressure of 1.8 bar

The equilibrium conversion, $X_{eq} = 0.79$

The corresponding equilibrium temperature = 62°C

At 0.07kg weight of catalyst, gas flow rate of 0.18m^3 , and gas pressure of 2.0 bar

The equilibrium conversion, $X_{eq} = 0.89$

The corresponding equilibrium temperature = 62.5 °C

From the result obtained in the graph of conversion, X_A against temperature

The optimum temperature and conversion can be determined by taking the average of equilibrium temperature and conversion

Therefore, for 1st 3 runs of temperature range 40 – 60

$$\begin{aligned}\text{Optimum temperature, } X_{op} &= \frac{0.62 + 0.69 + 0.77}{3} \\ &= 0.693 = 69.3\%\end{aligned}$$

$$\text{optimum temperature, } T_{op} = 43 + 44 + 44$$

$$\begin{aligned}& \frac{3}{3} \\ &= 43.7^\circ\text{C}\end{aligned}$$

For last 3 runs within temperature range of 60 – 80

$$\begin{aligned}\text{Optimum conversion, } X_{op} &= \frac{0.682 + 0.79 + 0.89}{3} \\ &= 0.715 = 71.5\%\end{aligned}$$

$$\begin{aligned}\text{Optimum temperature, } T_{op} &= \frac{62 + 62 + 62.5}{3} \\ &= 62.2^\circ\text{C}\end{aligned}$$

4.3 DISCUSSION OF RESULT

The rate of cracking, r_A of n-butane had been determined to be first order upon the plot of $-r_A$ against concentration, C_A .

The rate constant K had been determined to be different due primarily to the operating temperature and to an extent on catalyst weight, pressure drop and flow rate.

Within the temperature range of 40 – 60 °C. A rate constant of 1.65, 2.33 and 3.53 was obtained, while at a temperature between 60 to 80°C, a rate constant of 2.06, 3.29 and 3.91 was also obtained.

An Arrhenius plot (i.e. the graph of $\ln k$ against $1/T$) had been employed to verify the effect of temperature on the crackability of butane. The proportionate relationship between activation energy and slope had been determined.

Hence at temperature range of 40 – 60 °C. The activation energy is calculated to be 89.8 kcal/gmole which increases spontaneously as the temperature increases, due to side reactions.

From the graphical results obtained by plotting the conversion, X_A against temperature, T , equilibrium conversion and corresponding temperature had been determined. The value of optimum conversion and temperature for the two ranges of temperature was determined from the equilibrium conversion and temperature.

Therefore, the average equilibrium conversion and temperature for both ranges of the temperature (i.e. 40 – 60 °C and 60 - 80 °C) was found to be 69.3%, 43.7 °C and 71.1%, 62.5 °C respectively. This was taken as the optimum conversion and temperature.

The average equilibrium temperature and conversion is found to be the optimum temperature and conversion respectively.

CHAPTER FIVE

5.0 CONCLUSION

The following assumptions could be made why determining the optimum conversion of catalytic cracking of butane in a fluidized bed reactor.

1. The rate of cracking of paraffin, $-r_A$ (butane) is first order with respect to the reactant.
2. That the fluidization properties of fine powder like zeolite catalyst enhance the continuous transportation in the reactor.
3. That at slight temperature, weight, flowrate and gas pressure charge, there is proportionate change in rate constant and consequently conversion.
4. That the rate of conversion increases with increasing temperature till optimum conversion is obtained.
5. That the slight increase in conversion with increasing temperature after optimum value proved the endothermic nature of fluidized bed catalytic cracking.
6. That at different temperature range during catalytic cracking of butane, the average equilibrium conversion and corresponding temperature is considered the optimum conversion and optimum temperature respectively.
7. The linearity of rate constant, K with temperature (i.e. Arrhenius plot) has been employed to detect the influence of temperature on catalytic cracking of butane. And also found activation. Energy, E increases with slight increase in temperature.

5.1 RECOMMENDATION

- 1. Reactor with high degree of precision should be employed for subsequent experiment. This will enable a more precise and accurate determination of optimum conversion for gaseous hydrocarbon likes butane.**
- 2. The effect of pressure drop along the length of column of the riser, particle size of the catalyst, heat and mass transfer should be optimized in subsequent experiment. This will aid to measure the effect of the fluidization properties of catalyst during fluidized catalytic cracking.**
- 3. The work should be adopted on a commercial scale, to ensure its acceptability and hence quenching the ever increasing need for the production of polypropylene.**

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APPENDIX A

For S_1R_1 with temperature range (40-60⁰C) and S_2R_1 with temperature range (60-80⁰C)

Catalyst weight = 50g = 0.05kg

Pressure = 1.6 bar

Initial temperature = 25⁰C = 25+273 = 298 K

Flow rate = 2000cm³/min

1m³ = 10⁶ cm³; 1hr = 60min

$$\begin{array}{ccc} \frac{2000\text{cm}^3}{\text{min}} & \frac{60\text{cm}^3}{1\text{hr}} & \frac{1\text{m}^3}{10^6\text{cm}^3} \\ \frac{\text{cm}^3}{\text{min}} & \frac{\text{cm}^3}{\text{hr}} & \frac{\text{m}^3}{\text{hr}} \end{array}$$

$$= \frac{2000 \times 60}{10^6} \frac{\text{m}^3}{\text{hr}} = 0.12\text{m}^3/\text{hr}$$

1 bar = 10⁵ pa or Nm⁻²

$$C_{A0} = \frac{1.6 \times 10^5}{8314 \times 298} = 0.0646\text{molm}^{-3}$$

$$F_{A0} = C_{A0}V = 0.06456 \times 0.12$$

$$F_{A0} = 0.007752 \text{ mol/hr}$$

$$\frac{W}{F_{A0}} = \frac{0.05}{0.007752} \frac{\text{kg}}{\text{mol/hr}}$$

$$= 6.449948 \text{ hr. kg cat mol}^{-1}$$

APPENDIX B

For S_1R_2 with temperature range (40-60⁰C) and S_2R_2 with temperature range (60-80⁰C)

Catalyst weight = 60g = 0.06kg

Pressure = 1.8bar

Initial temperature = 25⁰C = 25+273 = 298 K

Flow rate = 2500cm³/min

1m³ = 10⁶ cm³; 1hr = 60min

$$\begin{array}{c} \frac{2500\text{cm}^3}{\text{min}} \quad \frac{60\text{cm}^3}{1\text{hr}} \quad \frac{1\text{m}^3}{10^6\text{cm}^3} \\ \swarrow \quad \quad \quad \swarrow \quad \quad \quad \swarrow \\ \frac{\text{cm}^3}{\text{min}} \quad \quad \quad \frac{\text{cm}^3}{\text{hr}} \quad \quad \quad \frac{\text{m}^3}{\text{hr}} \end{array}$$

$$= \frac{2500 \times 60}{10^6} \frac{\text{m}^3}{\text{hr}} = 0.15\text{m}^3/\text{hr}$$

$$1 \text{ bar} = 10^5 \text{ pa or Nm}^{-2}$$

$$C_{A0} = \frac{1.8 \times 10^5}{8314 \times 298} = 0.0646\text{molm}^{-3}$$

$$F_{A0} = C_{A0}V = 0.0646 \times 0.15$$

$$F_{A0} = 0.01091 \text{ mol/hr}$$

$$\frac{W}{F_{A0}} = \frac{0.06}{0.01091} \frac{\text{kg}}{\text{mol/hr}}$$

$$= 5.505 \text{ hr. kg cat mol}^{-1}$$

APPENDIX C

For S_1R_3 with temperature range (40-60°C) and S_2R_3 with temperature range (60-80°C)

Catalyst weight = 70g = 0.07kg

Pressure = 2.0bar

Initial temperature = 25°C = 25+273 = 298 K

Flow rate = 3000cm³/min

1m³ = 10⁶ cm³; 1hr = 60min

$$\begin{array}{c} \frac{3000\text{cm}^3}{\text{min}} \quad \frac{60\text{cm}^3}{1\text{hr}} \quad \frac{1\text{m}^3}{10^6\text{cm}^3} \\ \swarrow \quad \quad \quad \swarrow \\ \frac{\text{cm}^3}{\text{min}} \quad \quad \quad \frac{\text{cm}^3}{\text{hr}} \quad \quad \quad \frac{\text{m}^3}{\text{hr}} \end{array}$$

$$= \frac{3000 \times 60}{10^6} \frac{\text{m}^3}{\text{hr}} = 0.18\text{m}^3/\text{hr}$$

1 bar = 10⁵ pa or Nm⁻²

$$C_{A0} = \frac{2.0 \times 10^5}{8314 \times 298} = 0.0807\text{molm}^{-3}$$

$$F_{A0} = C_{A0}V = 0.0807 \times 0.18$$

$$F_{A0} = 0.01453 \text{ mol/hr}$$

$$\frac{W}{F_{A0}} = \frac{0.07}{0.01453} \frac{\text{kg}}{\text{mol/hr}}$$

$$= 4.82 \text{ hr. kg cat mol}^{-1}$$