Conversion of High-Molecular Weight Hydrocarbons to More Valuable Compounds by Nano Catalysts

A Thesis Submitted to the Department of Chemical Engineering, School of Chemical and Materials Engineering(SCME), NUST, Islamabad, in the partial fulfillment of the requirements for the degree of

Masters of Science (MS)
In
Energetic Materials Engineering

Submitted by

Ghulam Nabi
Registration Number: 2011 - NUST -MS PhD - EM-E-12
Supervisor Dr. Habib Nasir
Co- Supervisor Dr. Iram Mahmood

School of Chemical and Materials Engineering (SCME)
National University of Sciences and Technology (NUST)
H-12 Campus Islamabad

FORM TH-3

MASTER'S THESIS WORK

Final Oral Exam

Student's Name: Ghulam Nabi

Department: Chemical Engineering Department, SCME

Title: Conversion of High-Molecular Weight Hydrocarbons to More Valuable Compounds by Nano Catalysts.

Name of the Supervisor: Dr. Habib Nasir

ABSTRACT

This research focuses on cracking of high-molecular weight hydrocarbons to more valuable compounds using nano catalysts, solar energy and thermal energy. This research uses nano catalysts (characterized through SEM, EDS, XRD and PSA characterization techniques) and catalysts in bulk form as to analyze the difference in the products of nano and bulk catalysts. Naphtha cracking is carried under solar energy, at room temperature, using UV light and thermal energy. Variations in research techniques are meant to analyze the output from least input and advent latest trends in the field of petroleum. Degradation results obtained were analyzed with the help of GCMS.

Open to Public

Location: **SCME Seminar Hall** Date/Time: ______________

__________________ __________________ __________________

Thesis Supervisor **HoD** **Dean**

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ (1:1)

IN THE NAME OF ALLAH

THE MOST MERCIFUL

THE MOST BENEFICIENT

وَفَجَّرْنَا الْأَرْضَ عُيُونًا فَالْتَقَى الْمَاءُ عَلَى أَمْرٍ قَدْ قُدِرَ

(54:12

And We made the earth burst forth with springs and the waters met for a purpose that was preordained.

(Surah-Al-Qamar)

Certificate

It is certified that the entire work in the thesis i.e. "Conversion of High-Molecular Weight Hydrocarbons to More Valuable Compounds by Nano Catalysts" by **Mr**. **Ghulam Nabi**, for award of MS degree in Energetic Materials Engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan, is an original work and completed in our presence, guidance and supervision. Research work is authentic and fulfills the required criteria of MS.

Supervisor: ______________

Dr. Habib Nasir

Professor

School of Chemical and Materials
Engineering, NUST, Islamabad

Co-Supervisor:___________

Dr. Iram Mehmood

Asst. Professor

School of Chemical and Materials
Engineering, NUST, Islamabad

Submitted through

Principal/Dean: ______________

School of Chemical and Materials Engineering, NUST, Islamabad

Dedicated To

My

Dearest Family

And

My Mentors

Abstract

This research focuses on cracking of high-molecular weight hydrocarbons to more valuable compounds using nano catalysts in contrast to catalysts in bulk and by applying thermal and solar energy along with analysis at room temperature and under UV light. Research focuses on chalking out difference of cracking results with catalyst in bulk and in nano size and also source of heat applied or at room temperature. Therefore, samples were divided on the basis of catalysts involved, whether nano or bulk and on the basis of heat source (room temperature, tube furnace, under UV light and under sunlight). Initially naphtha samples were set at room temperature and by using catalysts in bulk and in nano form. Catalysts used were CNTs, Fe_2O_3, Al_2O_3, Graphene Oxide, MgO nano particles and in bulk, CuO nano particles and in bulk, TiO_2 nano particles and in bulk. At room temperature samples were examined at 0, 2, 4 and five hours. After which samples were set under UV light for 30 minutes using above mentioned catalysts in nano and bulk form (Graphene Oxide, Fe_2O_3 nano particles and in bulk, MgO nano particles and in bulk, CuO, ZnO nano particles and in bulk, Al_2O_3 nano particles and in bulk TiO_2 nano particles and in bulk). Naphta samples were then subjected to sunlight for 24 hours using above entire variety of catalysts in bulk and in nano form. At the end naphtha samples cracking was carried using tube furnace at 200 ^{o}C and at 500 ^{o}C, initially without catalyst and then with Fe_2O_3 as catalyst with same temperatures (200 ^{o}C and at 500 ^{o}C). Cracking results were analyzed using GCMS.

Acknowledgements

All praises to **Allah Almighty,** The Most Merciful and the Beneficent, you bestowed your unending mercy for the completion of this research.

Then I extend my deepest and sincere gratitude to my gracious and able supervisor Dr. Habib Nasir, who provided his guidance and supervision for completion of this work. I would like to thank my dissertation committee members Dr. Habib Nasir, Dr. Irum Mehmood, Dr. Arshad Hussain and Dr. Abdul Qadeer for their insightful thoughts, suggestions and guidance. I also thank to Dr. Uzaira Rafique from Fatima Jinnah Women University Rawalpindi for helping me to accomplish my research work. I would like to thank Dr. Mujahid and Col. Nadeem Ahsan for their support and encouragement.

My special thanks are for Pakistan Army in general and Pakistan Army Ordnance Corps in particular for detailing me to undergo MS from SCME (NUST). I also extend my gratitude to my respected seniors, my unit officers and colleagues who were always there to appreciate my work and encouraged me during the course of research.

I also appreciate the nice company of my class fellows; Major Muhammad Asif Khan, Major Safdar Hayat, Major Haris Mustafa, Mr. Shareef Ullah, Mr. Jamshaid Khan and Mr. Samar Abbas. I always cherish the happy moments spent with them.

(Ghulam Nabi)

Table of Contents

List of Figures

List of Tables

List of Abbreviations

EDS	-	Energy Dispersive Spectroscopy
FCC	-	Fluidized Catalytic Cracking
GCMS	-	Gas Chromatography Mass Spectrometry
GO	-	Graphene Oxide
PSA	-	Particle Size Analyzer
SEM	-	Scanning Electron Microscope
UV	-	Ultra Violet
XRD	-	X-Ray Diffraction

Chapter 1: Introduction

1. This chapter encompasses the details of crude petroleum their refining and further cracking into different desired deductions. In this segment information about the oils is discussed, their past and present techniques which govern their cracking.

1.1. **Crude Resources**

World is inching in every sector of life to comply with ideas and basic needs. To pursue the purposes energy/fuel (material which provides heat) plays a pivotal role. Fuels play an important role for energy generation in industries. Fuels can be classified in two categories; fuels which generate heat by simple combustion are known as "fuels" where as fuels which release energy by fission or fusion are known as "nuclear fuels" [1]. Fuels are classified as solid, liquid and gasses depending upon the state of their occurrence. Nature has gifted various crude resources to meet the routine requirements including energy. Demand and supply management has ushered mankind to develop novel ideas to fulfill the requirements. Every crude resource can have multiple uses, as of crude oil; used for energy source, petrochemical industry and is also used as precursors for other chemicals production. Nowadays ethylene and propylene are being used in the petrochemical industry as a feed stock for plastic, fiber and other organic chemicals [2-4]. These are ultimately consumed in packaging, transportation, construction industries, consumer markets and in multitude of other industries [5].

Petroleum (rock oil) occurs in nature from brown to black in color, mainly consists of hydrocarbons. These oils are either pumped out or they flow out spontaneously due to high pressure [1]. There are various theories relating to the formation of petroleum as:-

1.1.1. Carbide Theory

This theory states that petroleum contains hydrocarbon because of the water action on inorganic carbides. However carbides are resulted from the action of carbon and metals present beneath earth under intense pressure and temperature [1].

$$\mathbf{Ca + C_2 \rightarrow CaC_2}\ [1]$$

However, this theory could not give a satisfying response for the presence of sulphur and other chlorophyll like materials which are sole plant components.

1.1.2. Engler Theory

As per this theory petroleum belongs to animal origin [1]. This theory further states that petroleum is resulted from the decomposition of marine animals pressed under intense temperature and pressure. And this is being supported by the experimental work which is carried out by decomposing the fish oil and various other animal oils which decomposed to a product which is quite close to the natural petroleum. But this theory was unable to answer the presence of chlorophyll (green color product pertaining to plants) which is present in the natural oil.

1.1.3. Modern Theory

This theory states that petroleum is the fine product of both the marine animals and of forests of prehistoric era, which suffered the high temperature and extreme pressure [1]. As these both bio materials remained under that very condition for hundreds of years they converted into biological matter narrated as petroleum in present era. It is also mentioned here that only the sea plants resulted into petroleum, where as the land plants decomposed into coal. Due to the liquid state of petroleum, it might shift from one place to other. So there are bright chances that the petroleum being pumped from any place might not be of that particular place originally. Composition of petroleum in its percentage is as following [1]:-

- Carbon 84-87%

Hydrogen	11-15%
Nitrogen	0.1-1.5%
Sulphur	0.1-3%
Oxygen	0.3-1.8%

Primary components of petroleum are hydrocarbons (paraffins, aromatics, naphthalenes and olefins etc.) [1]. However brief quantities of sulphur, oxygen and nitrogen are the impurities along with few metals like vanadium and platinum.

1.1.4. **Difference Governing Origins of Coal and Petroleum Oil**

Petroleum oil is mainly produced from the sea plants and the animals and decay occurs at strong reducing conditions however coal is formed only from land plants which were subjected to bit mild conditions [1]. It is also noticed that coal deposits are found static where as petroleum products are not static due to the presence of high pressure and temperature conditions.

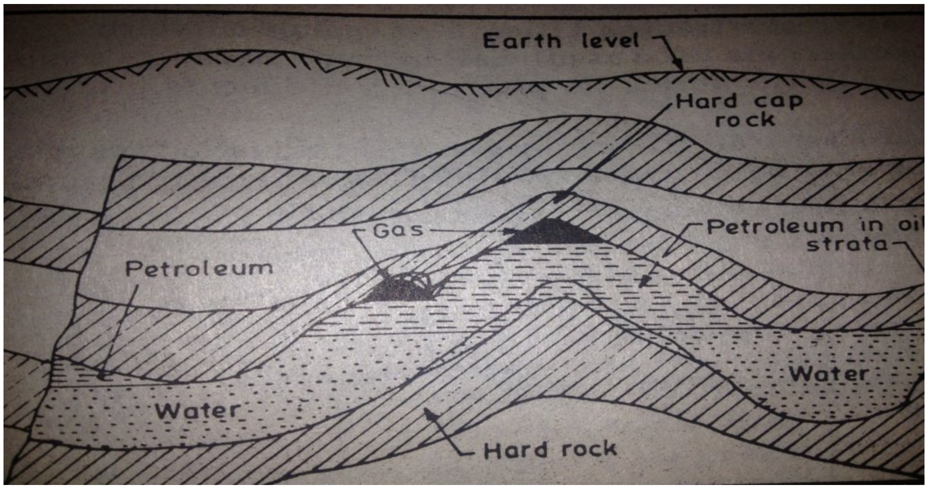


Figure 1.1: Typical Layout of Oil Reservoirs [1]

1.2. Petroleum Products and Their Modalities

Crude oil once drilled from its deposits is at first hand separated from gas products, made free from water sediments and free from salts and then at the end it is sent to the oil refineries (this separation process is called pretreatment) [1]. Crude oil once drilled out of oil well contains approximately 25% water, 2000 to 5000 mg/litre salts ($MgCl_2$, $CaCl_2$, NaCl etc.) and sediments up to 1-1.5%. Once petroleum reaches the oil refineries is then separated into further petroleum products by basic distillation process or some other auxiliary operations.

1.2.1. Basic Cracking Products on the Basis of Various Boiling Temperatures

Crude oil after preheat treatment is sent in industries for segregation into basic consumable products where they are heated at extreme temperatures and products (Table: 1.1) are segregated basing on their boiling temperatures [1].

Table 1.1: Petroleum Products Basing On Their Boiling Temperatures

Components	Approximate Boiling Range	Uses
Gases (1-4 Carbon)	_	Domestic uses like cooking
Gasoline/petrol (1-12 Carbon)	Upto 150 °C	Motor fuel
Kerosene (12-16 Carbon)	150 °C- 250 °C	Illuminant and fuel
Light gas oil (16-18 Carbon)	250 °C-300 °C	High speed oil diesel
Heavy gas oil (18-21 Carbon)	300 °C-350 °C	Diesel oil
Fuel oil (21 Carbon and more)	Above 350 °C	Fuel for furnaces

1.2.2. The % Distillation Products from Crude Petroleum

Although exact % of cracking products depends upon the location of the crude petroleum, however on the broader spectrum cracking products % [1] can be estimated (Table: 1.2).

Table 1.2: % Cracking Of Crude Petroleum	
Petrol – 18%	Gas oil – 12%
Naphtha – 6%	Lubricating oil – 12%
Kerosene – 10%	Wax – 9%
Diesel – 8%	Residue pitch – 25%

At the end of the distillation process of crude oil a residue petroleum is found at the bottom which is normally heavy oil. These heavy oils are then collected and are further subjected to cracking through multiple routes [6]. Moreover, tremendous consumption of light oils (light hydrocarbons) have resulted in the depletion of light crude resources as a result heavy hydrocarbons are studied in variety to lighten them [7-9].

Now, this research provides another venue for cracking of higher molecular weight hydrocarbons which are being wasted in the form of coal tar on the roads and other use less usages in the form of heavy oils etc. The main purpose of cracking is to produce gasoline out of gas oil; however olefins for petrochemical industry are also produced. It is also attempted to enhance the quality of petroleum. There are few techniques being devised to enhance the octane number of gasoline and cetane number of diesel. Octane number is the standard by which the performance of an engine is measured "octane number depicts that the fuel can withstand more compression and is defined as the percentage by volume of iso-octane in n-heptane mixture". Octane number can also be improved by the addition of Tetra Ethyl Lead (TEL). TEL is an excellent knocking agent. It is important to mention that Cetane ($C_{16}H_{34}$) number of diesel is opposite to octane number which is desired to ignite as soon as it reaches in the cylinder. The time interval between fuel injection and its ignition is called delay period. Cetane has very shortest ignition delay because of which its cetane number rating is 100. Whereas Methyl Naphthalene has too delayed ignition so its rating is 0. The cetane number can be defined as "percentage volume presence of cetane in cetane/α-methyl naphthalene mixture". Cetane number increases in the sequence as under:-

$$\text{Aromatics} \rightarrow \text{iso-Parafins} \rightarrow \text{Naphthene} \rightarrow \text{Olefins} \rightarrow \text{n-Paraffins}\ [1]$$

On contrary to above the octane number improves in reverse to cetane number. Hence, Crude petroleum which contains high octane fuel will surely be poor in cetane number rating.

1.3. Crude Resource Development Techniques

Primarily there are two types of petroleum cracking [1].

1.3.1. Thermal Cracking

In this type of cracking the fuel is subjected to high temperature 450 – 750^{o}C or more under pressure varying from 1-70 atmosphere whether under vacuum or at ambient conditions. The quality of product will solely depend upon the conditions applied.

1.3.2. Catalytic Cracking

This type of cracking incorporates a catalyst during cracking at variety of allied conditions. Application of high pressure reduces the octane number, whereas increase in temperature will result in abundance of yield. This type of cracking has attained dominance over thermal cracking because of less input (temperature and pressure) required and more output in both regards of quantity as well as quality [10]. Furthermore the yield obtained is rich in octane number.

1.4. Current Cracking Technique Used World Wide

Oil refining is much competitive and operationally complex industry. Fluid catalytic cracking (FCC) is widely used and most important cracking /conversion process, in the field of petroleum refinery [11-13]. In this technique heavy molecular weight hydrocarbons are converted to more useful petroleum products. Earlier petroleum cracking was used to be carried out through thermal cracking which is now fully replaced by catalytic cracking, as this process produces better quantity and quality in product, olefin gases produced during this type of cracking are more valuable than those produced in thermal cracking. Feed stock for FCC has 340 °C boiling point or more and having molecular weight 200 to 600 or more (this fraction of gasoline is named as vacuum gas oil/heavy gas oil). This cracking technique vaporizes and cracks the long chain hydrocarbons to short once. In this feed stock at high temperature along with mild pressure comes in contact with the fluidized powdered catalysts (solid catalyst placed in vessel comes in contact with liquid feed “liquid/gas” behaves as fluid).

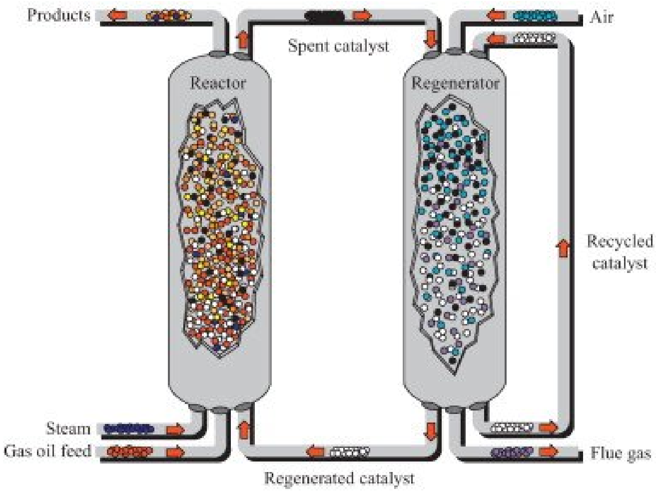


Figure 1.2: Fluid Catalytic Cracking (FCC) Unit Flow Diagram [13]

Reactor and regenerator play pivotal role in FCC unit. The catalyst accompanies feed stock at ratio 5:1, which becomes about 4.66 kg/litre of feedstock. An average FCC unit processes 75,000 barrels/day which require almost 55,900 tonnes of catalyst per day. Catalysts used in FCC have an average particle size from 60 to 100 µm. Catalysts used for cracking consist of crystalline zeolite, filler, binder, and matrix. Binder and filler provide physical strength to catalyst, whereas matrix component of FCC catalyst encompass amorphous alumina which allows larger weight molecules of hydrocarbon than the zeolites do. Here zeolite is the prime component having 15 to 50 weight% of entire catalyst. Zeolites used in FCC is known as Faujasite or type Y made up of silica or alumina tetrahedral, where each tetrahedron having either silicon or aluminum atom at the centre with tetra oxygen atoms attached at edges. Zeolite posses a sieve like structure from where only hydrocarbon molecules of 8-10 nm size can pass, hence resulting into the cracking of long chained hydrocarbons.

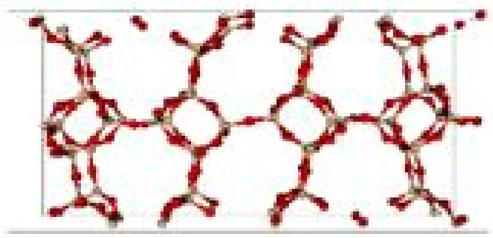


Figure 1.3: Zeolite Lattice Molecular Structure [14]

1.5. Solar Catalytic Cracking of Heavy Molecular Weight Hydrocarbons

1.5.3. Solar Energy

Photo catalysis has large application space to bend solar radiations which are omnipresent and abundant energy source. Renewable fuels are frequently used as easy source for energy, however their extreme use generates various serious nature problems like depletion of mineral deposits, release of green house gases and an increase in the amount of CO_2 [15]. It was therefore necessary to find an alternate of fossil fuels, which has the quality of easy availability, cheapness and no environmental hazards. And solar energy completes all above stated requirements. Solar energy is comprised of radiant (visible) light and the heat. Solar energy is the prime source of energy for all the requirements of life at our planet (Earth). Sun is the sole source of this tremendous amount of energy. Sun is composed of hydrogen, having extreme temperature which levels the ground for nuclear fusion. In hydrogen fusion two hydrogen nuclei fused in together and generate an atom of helium which results in tremendous amount of heat release. In 2002 it was calculated that our planet (earth) including land, rivers and oceans received a total energy of almost 3,850,000 exa joules (EJ 10^{18}) per year and the amount it received in one hour was more than the energy consumed in the entire year. Solar energy we receive in one year is calculated to be twice the total energy we can ever produce from earthy minerals. It is guessed that approximately 120 million tons of hydrogen is fused to form helium in just one minute. Hence this reaction provides ground for the supply of uninterrupted solar energy which is main source of life at our planet.

Sun dissipates energy equally in all directions and earth receives 1400 Watts/m^2. It is assessed that sun light consists of small ultraviolet, mainly visible (400 to 700 nm) and some infrared light. There is also a very minute amount of high energy possessing x-rays which are unable to penetrate the outermost layer of atmosphere around earth because of which they are not calculated during solar energy distribution. 400 nm wave lengths are detected as violet by our eye as 600 nm is detected red. However ultra violet rays have shorter wavelength than violet and infrared posses greater than red because of which these both types of rays manage to escape from our visibility. Infrared rays are perceived as heat energy which plays an important role for temperature on earth. The graphical distribution of sun light manifests that majority of solar energy consist of visible region. Figure: 1.4 illustrates the distribution of various energy regions.

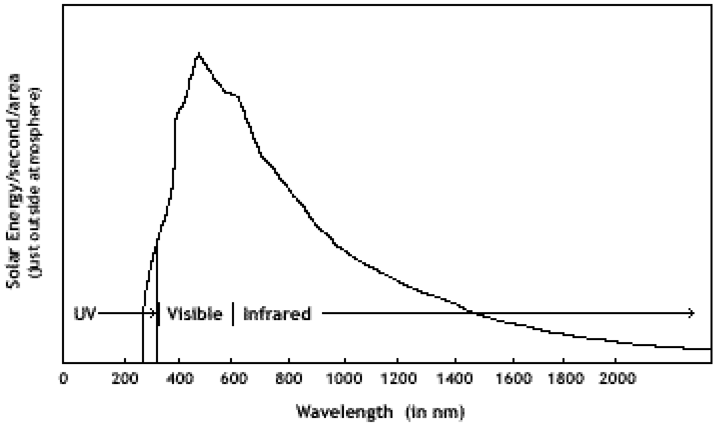


Figure 1.4: Depiction of Solar Energy Distribution [16]

1.5.4. Solar Energy Applications and Related Technologies

Technologies related to solar energy can be divided into two categories; active and passive solar technologies. In active solar technology solar energy is harnessed by various gadgetries (solar panels and solar auto mobiles) to other forms of energy.

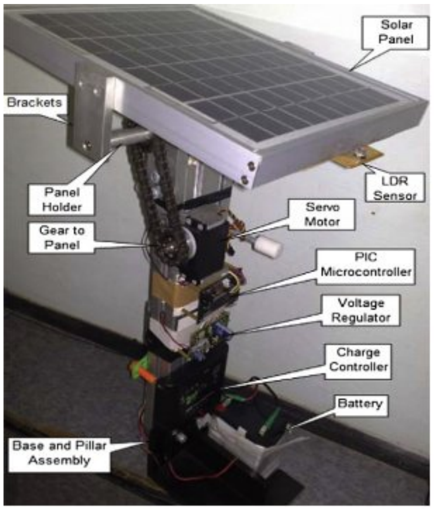


Figure 1.5: Active Solar Energy Devices [17]

On the contrary passive solar energy is normally related to building designs in order to circulate the air and sunlight. Passive solar energy technology is the best use of local solar energy for daily routine with the help of windows, door and ventilators etc.

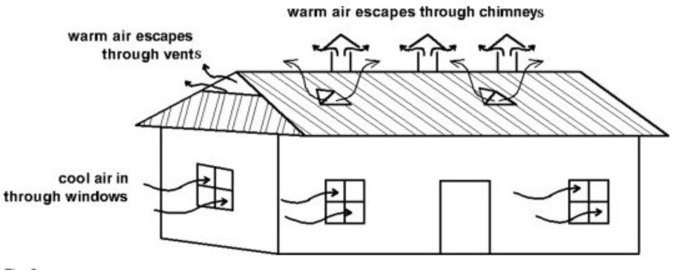


Figure 1.6: Passive Solar Energy Distribution [18]

1.6. Advent of Nanotechnology in Petroleum Cracking

Conventional processes can be given a boost by the advent of nanotechnology. Old processes required high reaction temperature and excess of pressures which resulted in high energy cost and emission of green house gasses. With the help of nano technology this problem can be resolved to a greater extent. Nano particles posses more surface area, greater porosity, high hardness, enough strength, more reactive sites and less decay probability. Therefore they are expected to result in much better yield in both aspects of quantity as well as quality. In this research few nano catalysts are being tried for cracking of naphtha using solar/thermal energy.

1.7. Naphtha

Naphtha is a broader term and is a mixture of liquid flammable hydrocarbons, comprising of lightest and most volatile fractions of petroleum. This segment of petroleum is primarily used for production of high octane gasoline, solvent and blending of motor fuel. It is also used in paint thinner as fuel gas (naphtha vapor) in steel plants for the production of H_2 (used for making of nitrogenous fertilizer). Naphtha is that segment of crude petroleum which lies between light gasses and heavy kerosene oils. Hydrocarbons mixture of naphtha lies between C_5 to C_{12} carbon atoms that include aromatics, olefins and paraffins having boiling temperature ranging from 30 ^oC to 200 ^oC. It also contains various salts, metals, sulphur and few other impurities. It appears colorless to radish–brown, similar to gasoline. Basically naphtha is used as a feed for producing high octane gasoline and for chemicals required in petrochemical industry.

1.8. Properties

Molecular weight of naphtha ranges from 100 - 215 g/mol, it posses 750 - 785 kg/m^3 density and Vapor pressure is less than 666 Pa (5 tor; 5 mmHg). Its boiling point ranges from 30 °C - 200 °C; light olefins C_5 to C_6 boil at 30 ^0C to 90 ^0C and heavy olefins C_6 to C_{12} boil at 90 ^0C to 200 ^0C.

Chapter 2: Literature Survey

2. This chapter deals with various literature reports which define different cracking techniques used for naphtha. It is worth to high light here that majority of petrochemical products are being produced by cracking naphtha through steam cracking at quite high temperatures. But in order to reduce the bulk of by products as well as enhance the selectivity of cracking different catalysts are being tried. It is also observed that this trend of introducing the catalysts has increased the cracking in many folds and has reduced the input of extra energy.

2.1. **Cracking Naphtha Thermally Using Nano Catalysts**

In this research CNTs were used as carrier for iron nano particles for thermally cracking the naphtha. And it was observed that result of cracking increased from 572 ^{o}C to 628 ^{o}C [5, 19]. As temperature is not as high as in commercial sector that's why the yield is also not as high as in industries, because the bottom line behind this all cracking part is that higher the temperature higher the cracking and increase in the yield of ethylene and propylene [1]. In this research it was also highlighted that the amount of iron nano particles played an important role i.e once the amount was raised from 0.34 weight% to 10 weight % the cracking result into ethylene and propylene was also raised but once it was further raised to 11.66 weight % it was observed that the product of ethylene and propylene started deceasing. It was also noticed that once weight % of iron nano particles was raised from 10% they (iron nano particles) started agglomerating and reduced its activity as active sites. It was also noticed that while keeping the conditions same and using CNTs alone as catalyst, the product was normal as if no catalyst was used. But once the iron nano particles were doped with CNTs the product of ethylene and propylene was noticed. In this research it is manifested that CNTs only cannot work in the cracking of naphtha vis-à-vis they act as an excellent catalyst supporter and a good heat absorber and can transform the heat in better way without forming any hot spot. Moreover, CNTs have got high porosity and specific surface area. Cracking of naphtha into ethylene and propylene was not found uniform on same temperatures as exhibited in Table: 2.1 [19].

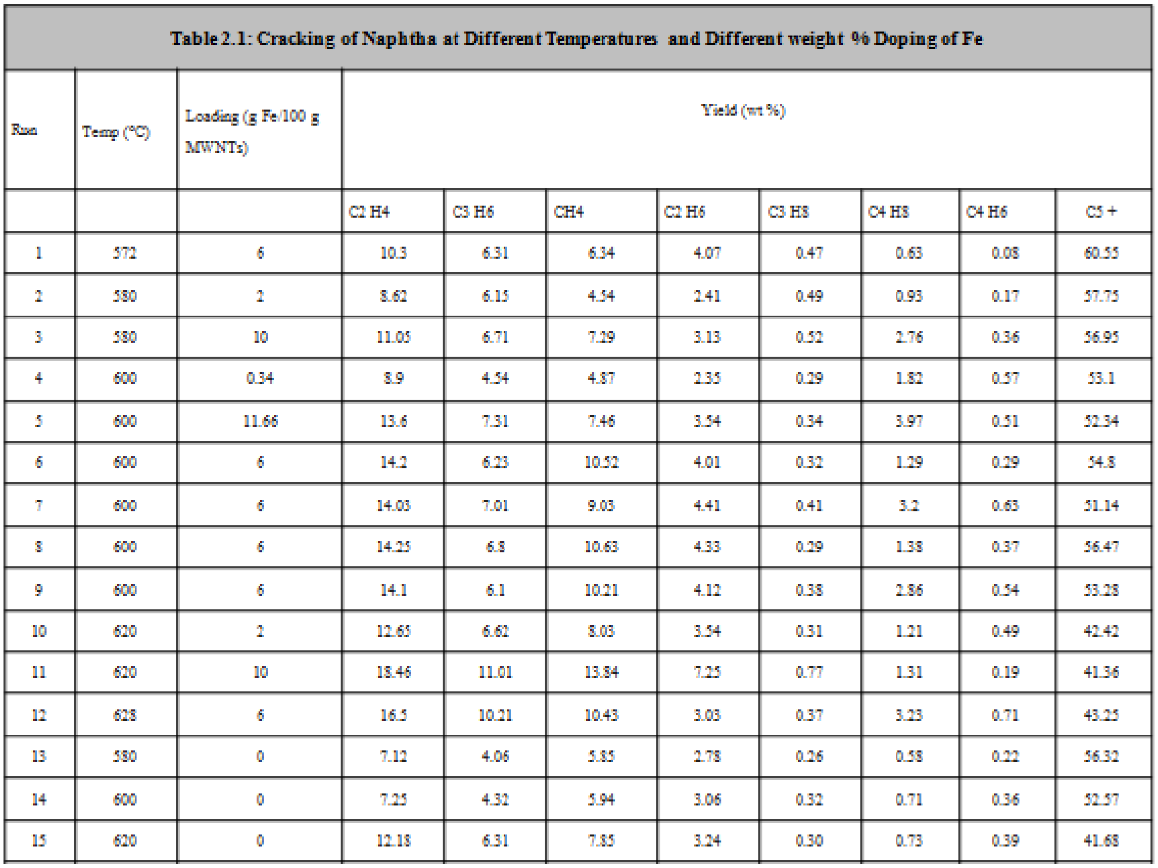


Table 2.1: Cracking of Naphtha at Different Temperatures and Different weight % Doping of Fe

Run	Temp (°C)	Loading (g Fe/100 g MWNTs)	Yield (wt %)							
			C2 H4	C3 H6	CH4	C2 H6	C3 H8	C4 H8	C4 H6	C5 +
1	572	6	10.3	6.31	6.34	4.07	0.47	0.63	0.08	60.55
2	580	2	8.62	6.15	4.54	2.41	0.49	0.93	0.17	57.75
3	580	10	11.05	6.71	7.29	3.13	0.52	2.76	0.36	56.95
4	600	0.34	8.9	4.54	4.87	2.35	0.29	1.82	0.57	53.1
5	600	11.66	13.6	7.31	7.46	3.54	0.34	3.97	0.51	52.34
6	600	6	14.2	6.23	10.52	4.01	0.32	1.29	0.29	54.8
7	600	6	14.03	7.01	9.03	4.41	0.41	3.2	0.63	51.14
8	600	6	14.25	6.8	10.63	4.33	0.29	1.38	0.37	56.47
9	600	6	14.1	6.1	10.21	4.12	0.38	2.86	0.54	53.28
10	620	2	12.65	6.62	8.03	3.54	0.31	1.21	0.49	42.42
11	620	10	18.46	11.01	13.84	7.25	0.77	1.31	0.19	41.36
12	628	6	16.5	10.21	10.43	3.03	0.37	3.23	0.71	43.25
13	580	0	7.12	4.06	5.85	2.78	0.26	0.58	0.22	56.32
14	600	0	7.25	4.32	5.94	3.06	0.32	0.71	0.36	52.57
15	620	0	12.18	6.31	7.85	3.24	0.30	0.73	0.39	41.68

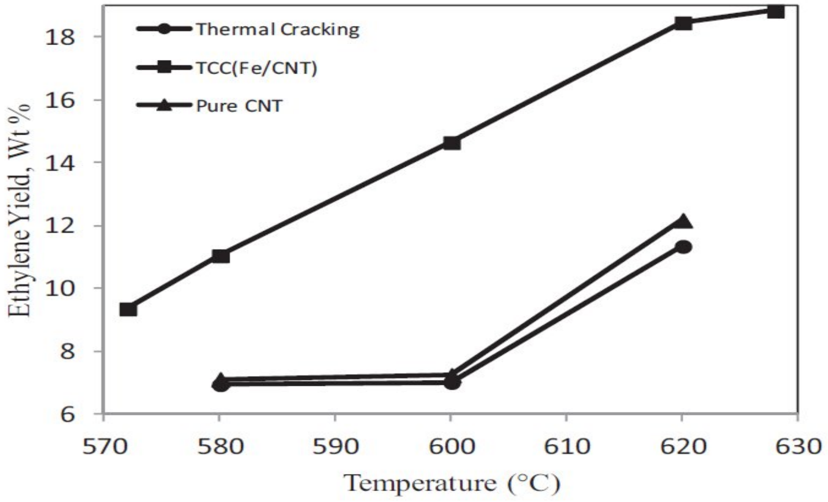


Figure 2.1: Ethylene Product vs Temperature [19]

2.2. Naphtha Cracking with CeO_2 Supported on CNTs Coated with SiO_2

Over a period of time various techniques, ways and means are being devised for the cracking of naphtha into maximum product and in best of its quality. Amongst all tried cracking techniques thermal catalytic cracking showed the best results. Working has been done on various chemicals in order to search out their mechanical, thermal properties and most importantly their surface area which plays a vital role in the cracking of naphtha. These all required qualities in majority are found in CNTs, which possess good thermal and mechanical strength and above all their surface area [19]. The readily and easily availability of CNTs and its low cast are also amongst its favorable factors. The tube like shape of CNTs plays an important role which gives an effect of confinement during reaction and accelerates the reaction rate which ultimately results in higher cracking rate. CNTs also favor in uniform transmission of heat without formation of any hot spot. Although the thermal resistance of CNTs is quite high even then it can be further enhanced by its coating, which is done here. Coating and doping of CNTs does not alter the shape and structure of CNTs [5].

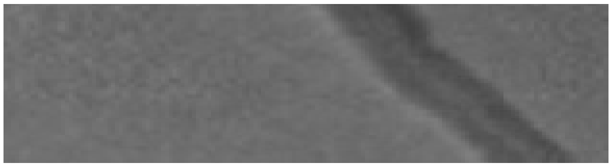


Figure 2.2: TEM Analysis of Fresh CNTs [5]

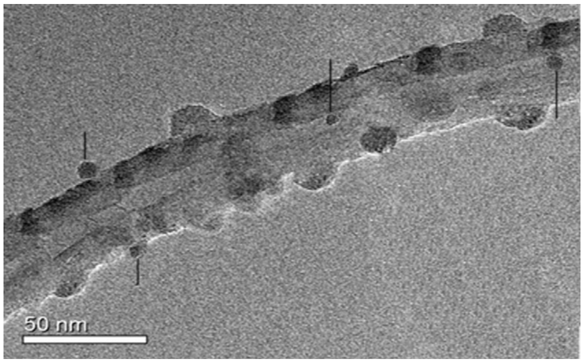


Figure 2.3: TEM Image of SiO_2-Coated and CeO_2-Deposited CNT [5]

On the other hand the thermal resistance of CNTs enhances in many folds once coated as exhibited at Figure: 2.4.

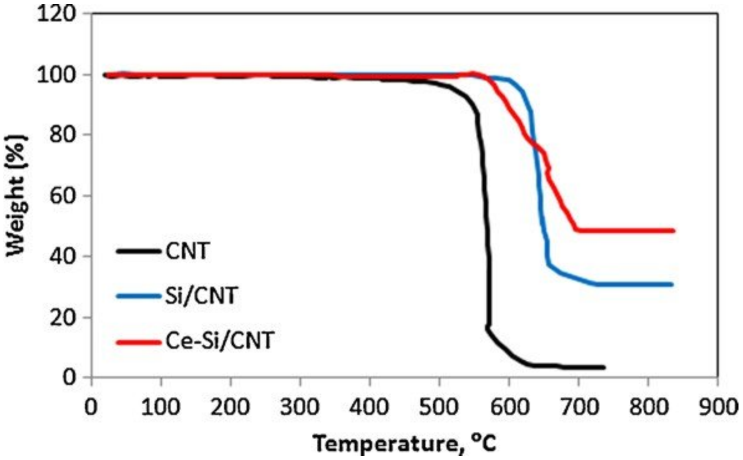


Figure 2.4: TGA Plots for Uncoated CNT, Si/CNT, Si–Ce/CNT [5]

It is also noticed that thermal cracking has increased from 24.12 weight % to 31.33 weight % [5].

2.3. Kinetic Study on Naphtha Cracking Using Fe/ZSM-5 as Catalyst

In order to meet the growing requirements of light olefins the process used is known as naphtha steam cracking. In this process HZSM-5 is used as catalyst which is doped with variety of Fe particles and that gives the product of 57.2 weight % with the reaction temperature applied as 600^{o}C. In this paper it is discussed clearly that by increasing the temperature the yield of ethylene will also increase and by calculating the product by objective data the margin of error to experimental data is till 12% [20]. More the lumps more the kinetic and experimental data are required. As to have two different lumps for ethylene and propylene the cracking trend can easily be predicted.

2.4. Fischer–Tropsch Naphtha Cracking

Fischer–Tropsch naphtha is naphtha produced by applying low temperatures and it is observed that this type of naphtha proves an excellent feed for the production of light olefins particularly ethylene. Cracking process used for this type of naphtha involves two boilers separately for naphtha and water which are preheated and then subjected to coil of 20 m length with the feed speed varying from 1 to 3 kg/h using an electronic pump. Effluent from here is separated into gas, liquid and water using condenser. Retention time is achieved/ enhanced by varying the flow rate of feed stock. Experiments were carried out with various operating conditions e.g varying feedstock flow rate and water flow rate along with variation in temperature etc. Experimental results manifested a very high yield of ethylene from the steam cracking of F-T naphtha, with the enhancement of yield till 41.83% under severe cracking conditions. These results indicate that F-T naphtha prove a healthy feedstock for the production of ethylene.

2.5. Thermal Cracking of Naphtha in the Presence of Carbon Dioxide and Steam

Till now it has been made quite obvious that ethylene proves a building block in the field of petrochemical industry [21]. Ethylene is a non-polar molecule and is an intermediate for the production of various chemicals like vinyl acetate and polyethylene as its production is easy and cheap. It also reacts with water and oxygen to produce various other chemicals. Ethylene is vastly used in the field of petrochemical industry so if any improvement made to enhance its product or to reduce its production cast may cause a great difference. Due to this numerous methods are being used by changing a variety of catalysts from gas to liquid. Domestic production of ethylene is carried out using gas and liquid catalysts; butane and naphtha. During the cracking coke formation is a problem of serious nature which restrict the heat transfer and renders the catalyst in effective as a result product selectivity is reduced. Aromatics (their condensation is the main cause for the coke formation) and unsaturated hydrocarbons prove precursor for the production of coke because of their rapid reactivity and attraction for radicals at very high temperature.

In this paper it is again highlighted that naphtha is a prime feedstock for the olefin production in furnace for pyrolysis. Initially naphtha is heated separately then steam and pressure are also applied and finally mixture is delivered in a chamber for preheat treatment till 616°C and 2.69 bars. From here the mixture of naphtha and steam is diverted to the reaction chamber where temperature is almost 900°C. Here in this paper steam is replaced by carbon dioxide as to observe the differences. It is observed here that the cracking is greater in case of CO_2 as a diluent because of the less coke formation which resulted in maximum heat transfer. It is clearly observed a 10% increase in the product resulted from CO_2 in comparison to the use of steam.

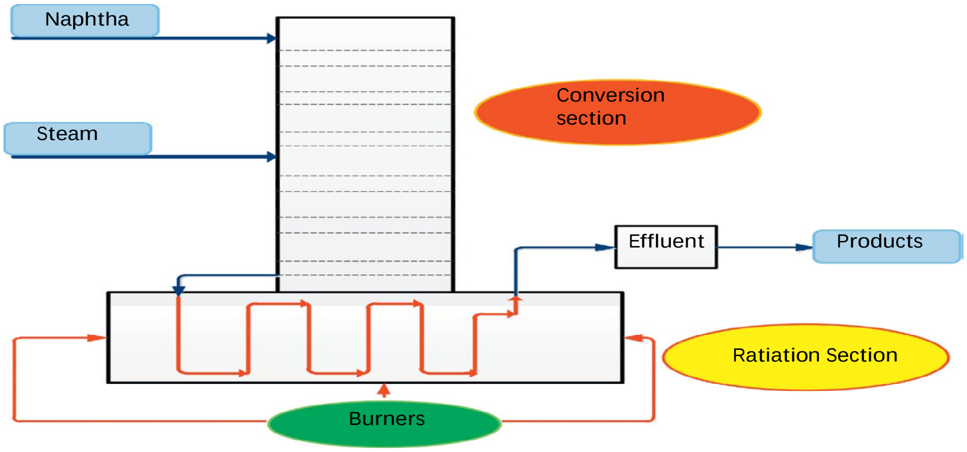


Figure 2.5: Furnace for Naphtha Cracking [22]

2.6. Fossil Fuel's Solar Decomposition a Sustainable Option

Currently world seems serious to switch energy from fossil fuel to hydrogen based energy if not on the nuclear energy as the 1st option. The project is based on interdisciplinary cooperation as material science and nano technology for reduction of production cost and other problems e.g. production, storage and distribution etc. Energy of sun can be multiplied to 10,000 suns by secondary concentration using non imaging optics [16]. Countries with abundance of natural gas can have great potential of hydrogen production by just decomposing natural gas. It also reduces the risk of CO_2 production once decomposed with solar energy. Hydrogen produced can be used for making ammonia and carbon black which can be used in the production of rubbers, tyres, polymers and batteries etc. Hydrogen is producible electrochemically, photo-chemically, photo-biologically and photo-electrochemically. However, production through solar thermo chemical process is much promising and also less hazardous with regards to green house gases from fossil fuels. The focal difference amongst conventional fossil fuel degradation and solar-thermal degradation of fossil fuels is the heat source. In conventional process source of heat is the combustion of fossil fuel and air, while in solar thermo chemical degradation process it is concentrated solar energy. The natural gas steam reforming is the major hydrogen production technique used in industry, which is practical and economical process to meet market demands relating to hydrogen. Steam reforming of natural gas is endothermic process which utilizes natural gas with air for combustion to high temperature which breaks carbon-hydrogen atoms covalently bonded with in methane molecule. 1 ton H_2 production would require consumption of 2 ton CH_4 which results in the generation of 5.5 ton CO_2. And for entire process additional 30% CH_4 is needed to burn for providing heat to the system. Hence 1 ton H_2 production is associated with 2.6 ton CH_4 which ends at release of 7.3 tons CO_2 into atmosphere. Hence, conventional hydrogen production method from natural gas steam reforming causes pollution in the atmosphere along with depletion of natural reservoirs [16, 23].

2.6.1. Concentration System for Solar Radiation

High temperature from solar energy can be achieved which depends upon solar collector's optics configuration and solar receiver's design. For optical configuration of solar collectors there are three configurations: tower, dish and trough. In this trough is low concentration technology with single axis tracking and only 400 – 450 ^{o}C temperature can be achieved.

2.6.2. **Solar Tower**

It is a tower which houses reflectors or receivers at top. Tower is centered by heliostats also called Fresnel reflectors. Reflectors are set in the field and set to harness the solar energy to the receiver located at solar tower's top. Receiver receives the solar radiations and uses its energy in the process. There is also a receiver down technology to which reflectors direct the sunlight which is located at the ground and easy to maintain and also less costly. However in this entire process energy can be multiplied from few hundreds to thousands which would be a very high temperature inside. The efficiency of tower mainly depends up on the components of tower: reflectors, receivers and power generation plants.

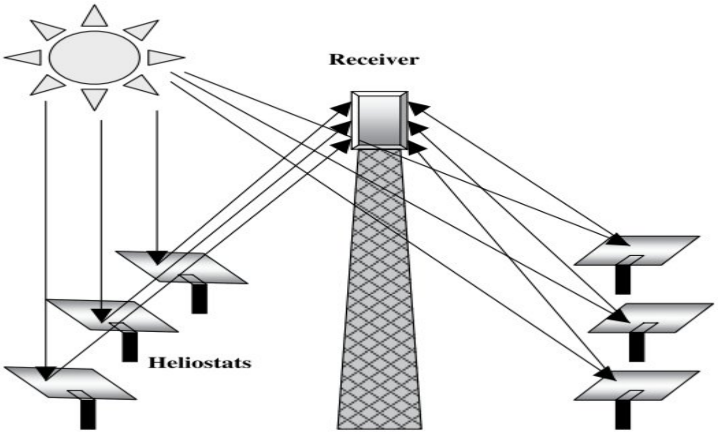


Figure 2.6: Solar Tower for Power Generation [16]

2.6.3. **Parabolic Dish**

In this system receiver is placed at focal point and optical axis directing sun rays are facing to sun [24]. Parabolic dish collector has the highest result amongst all other solar methods reaching to output of 10,000 suns [16]. More over parabolic dish is mobile with respect to the movement of sun where as solar tower is static.

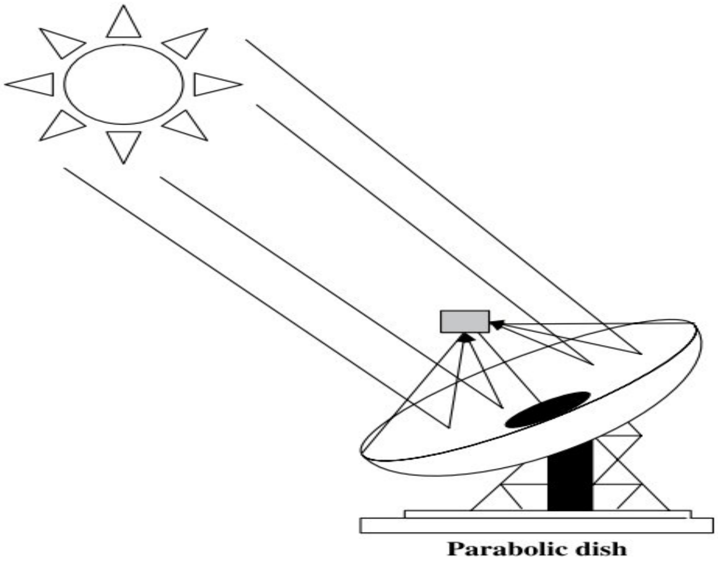
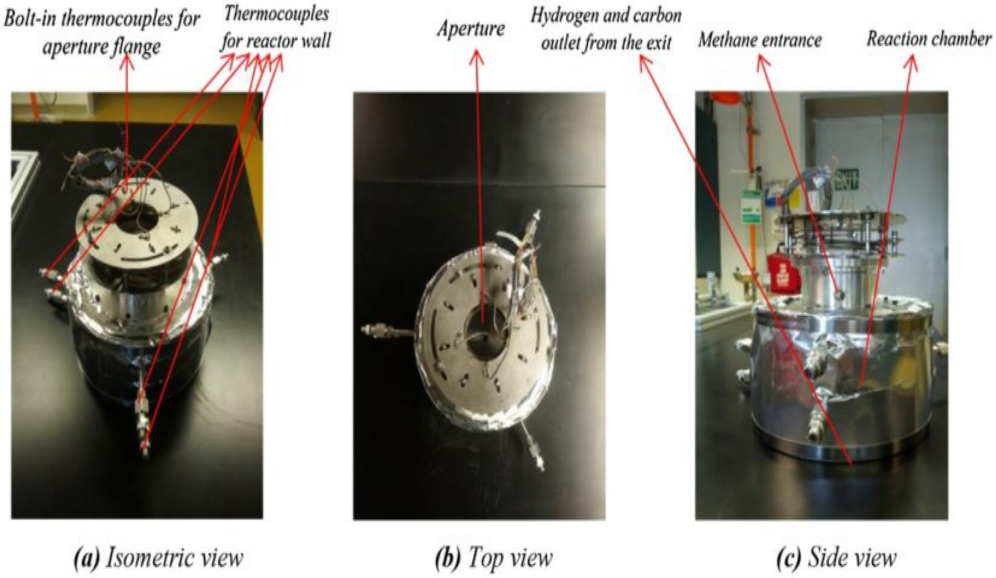


Figure 2.7: Parabolic Dish for Power Generation [16]

2.6.4. Solar Cracking for Hydrogen Production through Solar Reforming

Solar gasification and solar reforming for hydrogen generation from hydrocarbons can be carried. The carbon produced in this process is also marketable hence handsome amount can be earned in regard too. Carbon blacks demand is increasing on daily basis as it will be 11 M tons in 2011 [16]. 0.75 kg carbon black can be achieved by cracking single kg of natural gas. Two main products hydrogen and carbon black can be obtained via solar cracking. One kg of hydrogen generation results in three kgs of carbon black.



(a) Isometric view (b) Top view (c) Side view

Figure 2.8: Solar Reactor [15]

2.6.5. Summary

Above entire experimental discussion can be summarized as under:-

- Fuel consumption can be reduced using solar energy.
- End of green house gases [25].
- Pure hydrogen product: free of contamination.
- High grade of black carbon achieved.
- High chemical reaction due to direct irradiation.

2.7. Heat Transfer and Kinetic Analysis of Carbon Catalyzed Through Solar Cracking

Hydrogen in these days is used in different industries for cracking of hydrocarbon for the production of methanol and ammonia etc. Till now hydrogen is not being used as an alternate source of energy. Currently steam methane cracking for hydrogen generation is used which gives one kg of hydrogen along with almost 11.9 Kg of CO_2. In order to avoid the production of CO_2 there is another method known as solar thermal cracking of methane which generates hydrogen and carbon black. Carbon black produced here is of commercial grade.

$$CH4 \rightarrow C \text{ (solid)} + 2H2,\ \Delta H_{298} = 75 \text{ kJ/mol } [15]$$

Like every other cracking process above cracking also requires some energy which can be provided through concentrated solar energy. Through this process product can be obtained are 92% pure. This solar reactor is hanged at a focal point of concentrated solar reflectors [15]. Cylindrical body of reactor is located at top where methane gas is injected. Reactor body has quartz window in its cavity shaped body from where solar energy enters. Due to direct entry of sun light on reacting materials the temperature is too high. Therefore another secondary gas is introduced to reduce the temperature of window, this process in known as Tornado Flow Reactor. Refineries using catalysts benefits with regard to energy supply, normally it requires 1300 ^{o}C to crack methane while it just needs 600 - 950 ^{o}C. It also gives 100 % selectivity with regards to hydrogen generation and production of carbon black. Carbon black further facilitates in methane cracking as it absorb heat from reactor walls and transfers it to cracking process, hence increasing cracking in totality.

2.8. Summary of Literature Survey

Energy being the route for development in any field of science and oil being the prime source of energy, tremendous amount of work has been done and is being done to improve its quality and quantity. Till now majority of work for oil purification was carried using catalyst in bulk form, but now this trend is on its way to shift from bulk to nano regime. Moreover, the energy source for cracking is being shifted from fossil fuel to solar energy being tremendous in amount, safe and omnipresent. In the literature survey it is clearly observed that the quality and quantity both improve if the catalyst is of nano regime, using solar energy benefits in its cheapness and pollution free atmosphere.

Chapter 3: Experimental Techniques

3. This chapter describes different characterization techniques used for the investigation of ultimate achieved product. Here input for these experimental equipments is also highlighted. Environment required for these techniques, their working condition along with their working principal are also mentioned too.

3.1. **Particle Size Analyzer (PSA)**

This experimental technique as quite obvious from its nomenclature assists to determine the particle size of sample prepared in powder form and dissolved in any suitsable solvent. This technique is very much fruit full in numerous fields of industry ranging from mining to agriculture and chemistry to forestry. Particle size lying between 0.02 to 2000 microns can be examined. Particle size analyzer used at SCME, NUST is LA-920 of HORIBA Japan.

3.1.1. **How PSA Works**

Principle followed by PSA is laser/ light scattering. This technique is purely a physical phenomenon which reads the particle size of suspended stuff in suspension. By the help of this very technique the particle size or mean particle size of sample is determined.

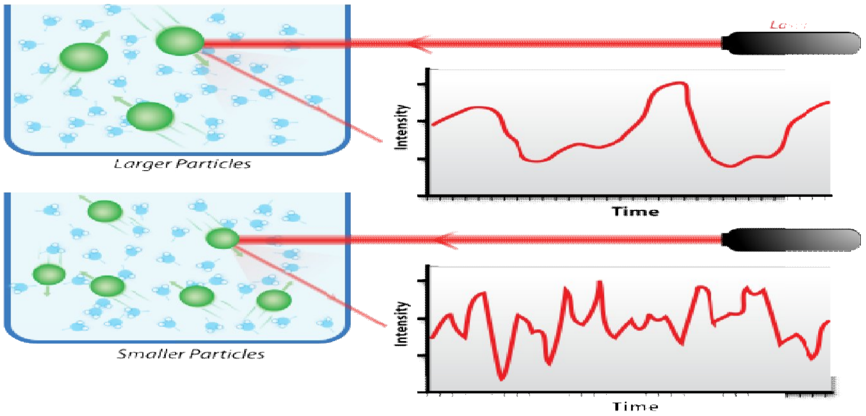


Figure 3.1: Working Principle of PSA

3.1.2. **Sample Preparation**

1 mg of graphene oxide was added in 500ml ethanol which was sonicated for 30 minutes. On the complete homogenous suspension of sample into ethanol 200 ml of sample was introduced into analysis chamber for its complete particle size examination.

3.2. Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) is an instrument which manifests the sample's image by a concentrated beam of electrons fired at the surface of the sample. The electron beam probes the sample surface and in retrospect an image is fabricated giving details of sample surface topography and details of its composition. The image of the sample surface comes instantly on reaching back of scattered fired electrons. The electron beam hits the atoms of the sample at the surface. SEM used here at SCME (NUST) was JSM-6490 A Analytical Scanning Electron Microscope of JEOL Japan. And the cotter used is JFC 1500 Ion Sputtering Device 250 Å Gold cotting GEOL Japan.

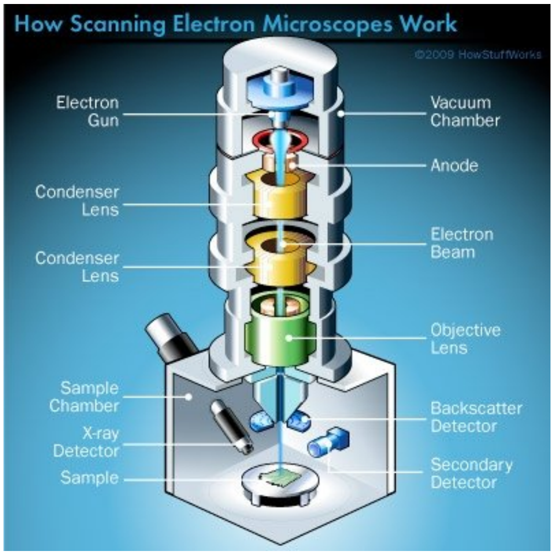


Figure 3.2: Schematic Diagram of SEM

3.2.1. **SEM Working Principle**

SEM generates a variety of signals from secondary electrons to back scattered ones and from transmitted electrons to x-rays. However SEM is not equipped with the detectors of each signal separately rather they all are detected by only single detector which is Secondary Electron Detector. Sample composition and its elemental form is pronounced by back scattered electrons because it is solely related to atomic number of sample. However, secondary electrons give the detailed information regarding the sample's surface and its morphology.

3.2.2. **Sample Preparation**

Sample preparation for the SEM varies for various sorts of samples. As for graphene oxide a pallet was prepared using pressing machine because a copper disc is used as carrier of sample once it is subjected to analyzing chamber of SEM. And to place the sample on the top of that copper disk of 2 mm thickness and having a diameter of 13 mm. A carbon tape adhesive is applied for holding the disc and sample together, which may give away a mixed signal once graphene oxide powder is placed on it. Therefore a pallet of graphene oxide is made and is coated with gold to make it conductive.

However, for MgO, ZnO and TiO_2 a very brief quantity of sample is dissolved in methanol and sonicated for 2 hours for better dispersion. Finally a drop of suspension is placed on the glass which is then subjected to analyzing chamber for detailed investigation. Said samples can even directly be placed on the carbon tape adhesive for further investigation.

3.3. **X-Rays Diffraction (XRD)**

XRD is a technique used to determine the crystal structure of given sample, measure spacing between inter layer or inter atomic rows and figure out the orientation of a crystal or a grain. XRD measures the internal stress of a limited crystalline regions, it also provides information about the shape and size of a crystal. This technique is called as XRD because atomic planes present in a crystal force the X-ray beam to interfere with each other once the beam of X-ray hit the crystal region and as a result the beam diffracts on the crystals present. These are electromagnetic radiations with the wave of 10^{-10}, occupying the gap between Gamma-rays and ultra violet waves. This technique is quite helpful in sample determination vis a vis it is a non destructive technique with regard to sample analysed. This technique is being used almost in every field of science in some way or the other.

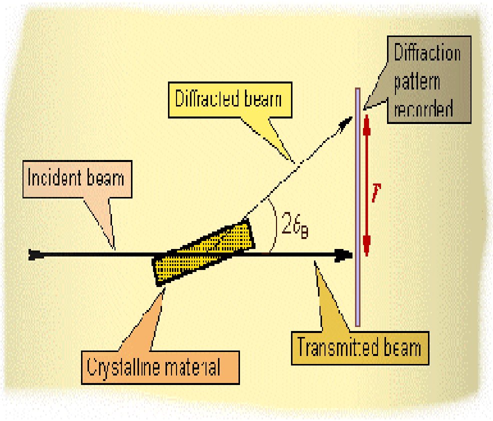


Figure 3.3: Exhibition of XRD Phenomenon

3.3.1. Working Principle of XRD

XRD works on the principle of measuring the diffraction angle after the X-rays leaves the sample, which make a certain pattern of peaks which is analyzed using Bragg's Law.

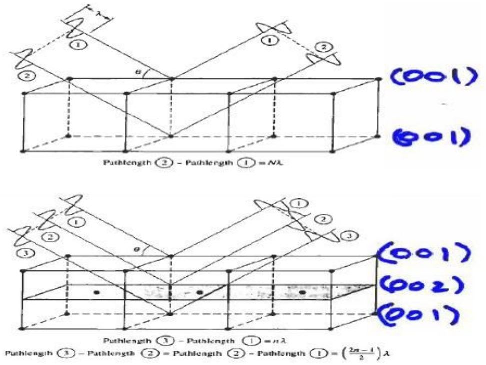


Figure 3.4: Behavior of X-ray Beam on Crystal Plane

3.4. Gas Chromatography–Mass Spectrometry [GCMS]

This analytical technique is used to examine the test sample may it be gas or liquid by using chromatography or by using the mass spectrometry in order to identify the constituents of the sample. GC-MS is a helpful investigating tool used at various corridors by probing agencies for the detection of explosives, drugs, chemicals and for environmental analysis.

GCMS comprises of two components 1st gas chromatograph and 2nd mass spectrometer. GC mainly hovers around capillary column, its different dimensions (diameter and length etc) and the phase properties. The interaction of two (mobile and stationary) phase will determine the separation quality, higher the retention time of mobile phase on stationary phase higher the separation of molecules and vice versa. When elute comes out of the stationary phase it is identified basing on its mass by mass spectrometer. Mass spectrometer breaks the molecule in ionized form and detects these ions on the base of mass to charge ratio. Both the detecting facilities (gas chromatograph and mass spectrometer) strengthen the detection because only single facility cannot do enough in detection of sample. Gas chromatograph (uses flame ionization detector) cannot detect the sample if ample of the molecules come together for the identification after passing through the column as they are having the same retention time. However, mass spectrometer requires a pure sample. It is almost impossible that both characteristics: cracking and retention time are same for two different molecules. So this fusion of mass spectrometer and gas chromatograph make a fine detection which is highly accurate.

GCMS used in this research is of SHIMADZU (Japan) GCMS QP 2010 ULTRA.

Figure 3.5: GCMS Display

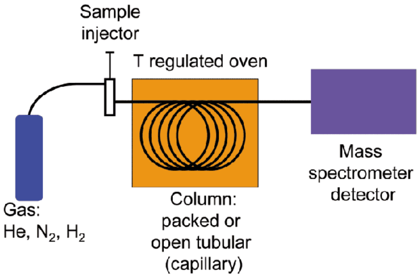


Figure 3.6: GCMS Functional Skeleton

3.5. Tube Furnace

Tube furnace an electrical heating apparatus is widely used in petrochemical industry, oil refining, fibers and chemical industries. It is the most widely used reliable apparatus available having controlled parameters of heating/cooling rates with uniform temperature control. The material flow (gas/liquid only) within the tube fitted in the furnace is heated up to desired temperatures. A critical temperature is accompanied and then cooled to ambient temperature at ranging cooling rates to make other required experiments. With these processing heating conditions, oxidation, decarburization and other unwanted reactions may occur within the material and surrounding atmosphere. Therefore, proper controlled atmosphere selection with processing conditions is extremely critical to achieve bright and accurate results. Heating coils are entrenched in thermally insulating matrix. Temperature of these coils can be regulated through thermocouple principle. Molybdenum disilicide, a new material has been incorporated in the heating apparatuses (certain Vecstar models only) that can produce a working temperature till 1800 °C. For a minimum air disturbance within the furnace, inlet and outlet of furnace are of minimum diameter which just allows the tubes to pass from within. Materials used in these reaction tubes are of fused quartz, alumina and Pyrex. Tube furnace used at Heat Treatment Lab of School of Chemical and Materials Engineering [SCME], NUST, is MTI Corporation: GSL.1600X40 USA.

Figure 3.7: Tube Furnace

Chapter 4: Experimental Work

4. This chapter will encompass the experimental set up for the cracking of heavy molecular weight hydrocarbons to lighter ones using two different set ups. One cracking in the presence of sun light and other using tube furnace for application of high temperature. Results obtained in both of these techniques will be discussed in the upcoming chapter.

4.1. Materials Used in Study

To proceed with experimental work and carry out various experiments purity of precursors (Table: 4.1) was given ultimate importance.

Table 4.1: Materials Used in Different Experimental Work

Precursors	**Purity %**	**Mean Particle Size**	**Remarks**
$Al(NO_3).9H_2O$	>99%		Merck
$(NH_4)CO_3.H_2O$	>99%		Merck
$Cu(CO_2CH_3)_2$	>99%		Merck
$Fe(NO_3)_3.\ 9H_2O$	>99%		Scharlau
NaH_2PO_4	>99%		Scharlau

4.2. Preparation of Fe_2O_3 Nanoparticles

Fe_2O_3Nanoparticles were prepared by hydro thermal method with following steps involved:-

- 3.2 ml of Fe $(NO_3)_3$. $9H_2O$ and 2.8 ml of NaH_2PO_4 were mixed

- Volume of sol was raised to 80 ml
- Vigorous stirring for 10 min
- Transferred into stainless steel Autoclave
- Aged for 48 hrs at 220 ^{O}C
- Then solution was sent for centrifuge and at end dried in vacuum oven at 50 ^{O}C

4.3. Characterization of Fe_2O_3 Nano Particles

Fe_2O_3 nano particles achieved by above said method were characterized by variety of following characterization techniques:-

4.3.1. SEM Result of Fe_2O_3

SEM image (Figure: 4.1) confirmed that the Fe_2O_3nano particles are cubic and uniformly dispersed with particle size ranging from 8.25 - 18 nm.

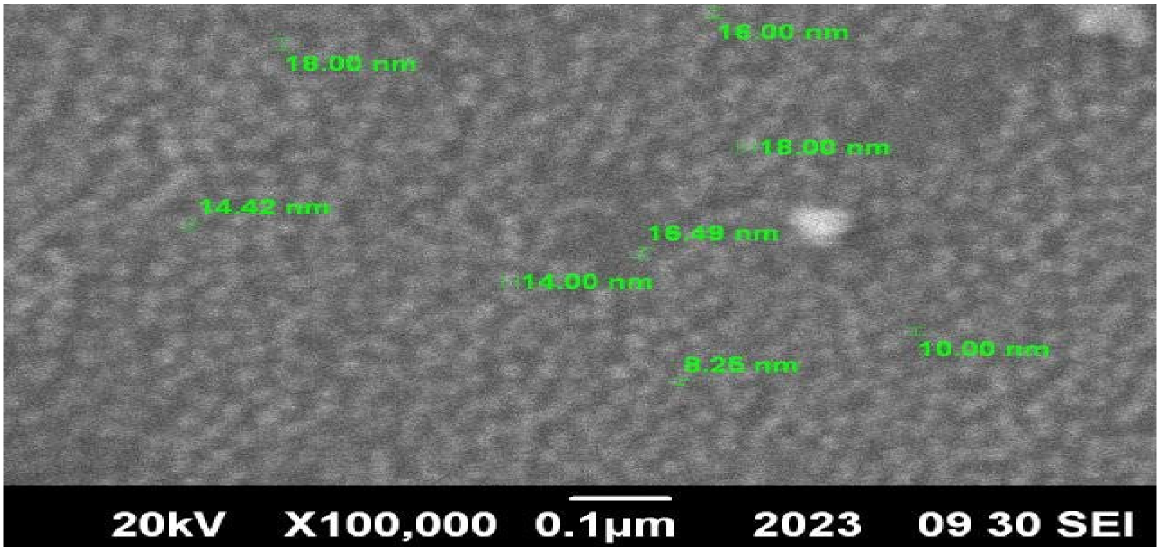


Figure 4.1: SEM Image of Fe_2O_3 Highlighting Particle Size (8.25 - 18 nm)

4.3.2. **XRD Results of Fe_2O_3**

XRD analysis of synthesized Fe_2O_3 was carried out in order to confirm the purity, crystallite size, crystal system and hkl values. XRD peaks (Figure: 4.2) matched and confirmed to stick pattern 01-089-7746. The peaks emerged at 2θ values 36.377, 42.609, 62.924, 74.354 and 78.743 corresponding to (110), (200), (220), (311) and (222) family of planes. The crystal structure found as Fm-3m Cubic and density 3.56 g/cm^3 which also confirms to pure Fe_2O_3.

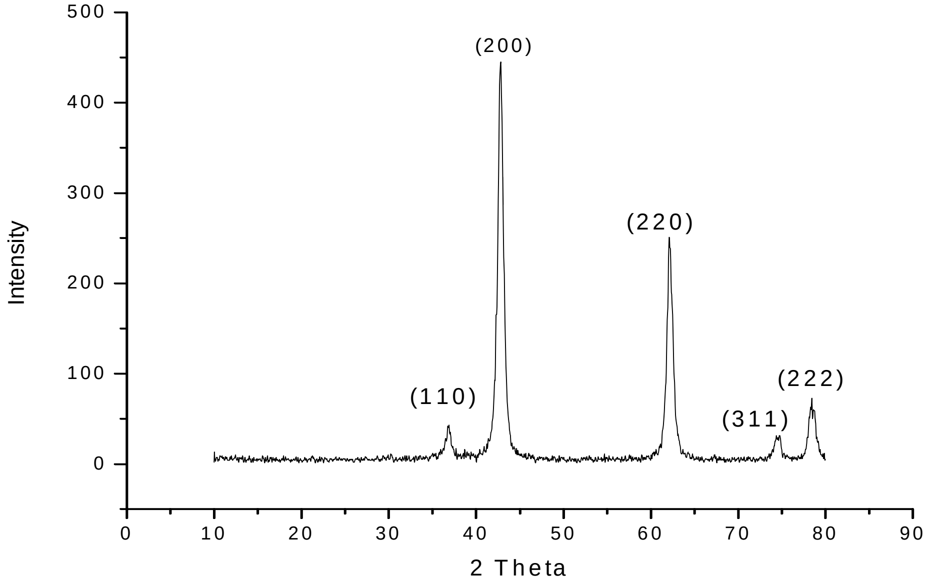


Figure 4.2: XRD Result of Fe_2O_3 Showing hkl Values

4.3.3. **Particle Size Analysis of Fe_2O_3 in Bulk Form**

Fe_2O_3 in Bulk Form was purchased from open market of Merck having average particle size of 26.06 µm.

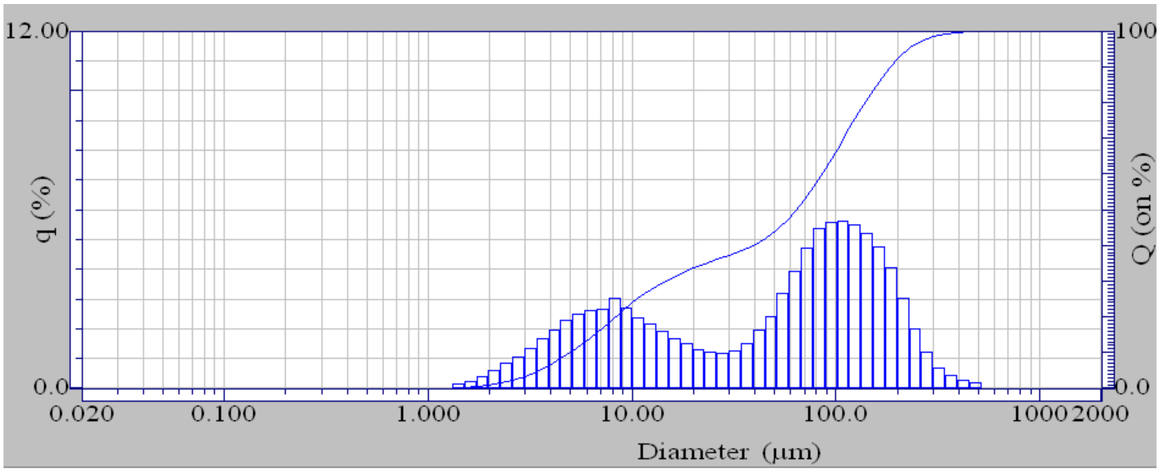


Figure 4.3: PSA Fe_2O_3 Bulk (Average Particle size – 26.06 µm)

4.4. Chemistry Involved For the Preparation of CuO

CuO nano particles were synthesized by Simple Precipitation Method.

- Preparation by simple precipitation method at different temperature conditions varying from 10 ^{O}C to 115 ^{O}C.
- Crystallize and crystallization increases with temperature.
- Using copper acetate Cu $(CO_2CH_3)_2$ as starting material.
- Application of ultrasonic radiations.
- Formation of CuO nano particles at 60 ^{O}C starts.

4.5. Characterization Techniques Used for CuO

CuO is also characterized in same mentioned corridors for ease in discussing the obtained results.

4.5.1. **SEM of CuO**

SEM analysis of CuO was performed to determine the nano particle size (Figure: 4.4) and it was revealed that sample particle size ranged from 42.69 - 86.67 nm and Tetrahedral in shape.

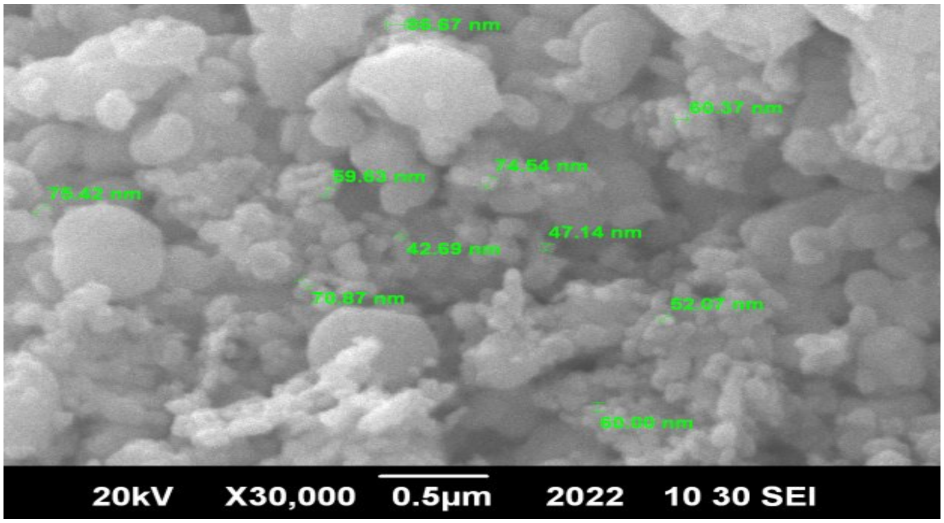


Figure 4.4: SEM Image of CuO Nano Particles (42.69-86.67 nm)

4.5.2. **PSA Result of CuO Particles in Bulk**

Bulk particles of CuO were brought from market of Merck as to have ease in comparing the results of catalysts in nano and the catalysts used in bulk.

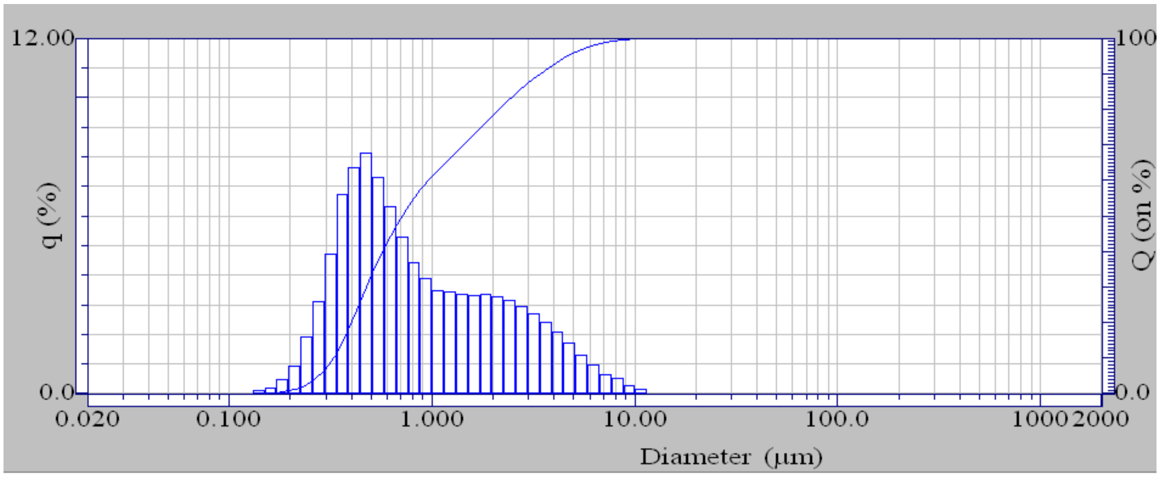


Figure 4.5: PSA CuO Bulk (Average Particle size – 2.73 µm)

4.6. Experimental Set Up for Al_2O_3 Preparation (Chemical Precipitation Method)

Al_2O_3 Nano particles were synthesized using chemical precipitation method by following below stated method:-

- 1 Mol/L Al $(NO_3).9H_2O$ and 0.16 mol/ L Ammonium Carbonate (NH_4) $CO_3.H_2O$.
- Reacting at 40 ^OC, kept on stirring for 15 min.
- Then left for 24 hours.
- Dried in vacuum at 80 ^oC for 8 hrs.
- Washed many times with distilled water and dried.
- At the end calcinated till 800 ^OC for 1 hr

4.7. Characterization of Al_2O_3

Various characterization techniques are used as to exactly examine the resulted product. Analysis hovers over its crystal size, structure and its constituent elements.

4.7.1. SEM Image of Al_2O_3

SEM analysis performance exhibited that nano crystals formed were body centered Tetrahedral in shape and their size ranged between 14 to 20 nm (Figure: 4.6).

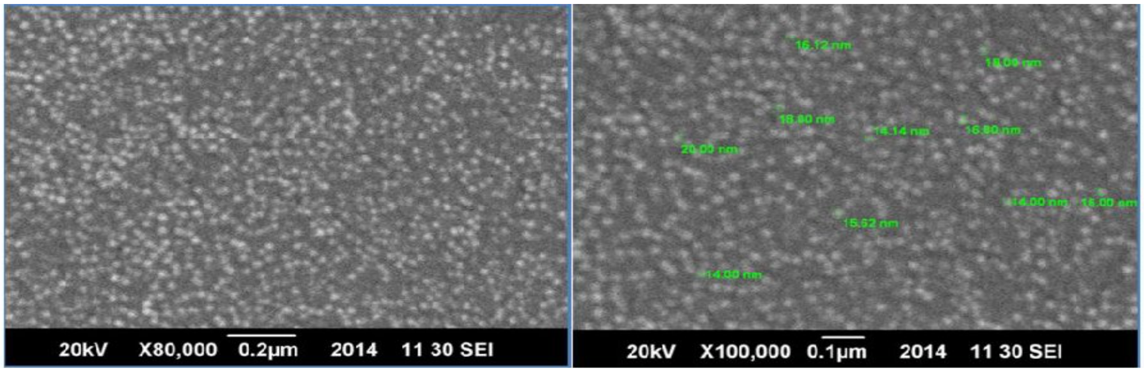


Figure 4.6: SEM Images of Al_2O_3 (14-20 nm)

4.7.2. XRD Results of Al_2O_3

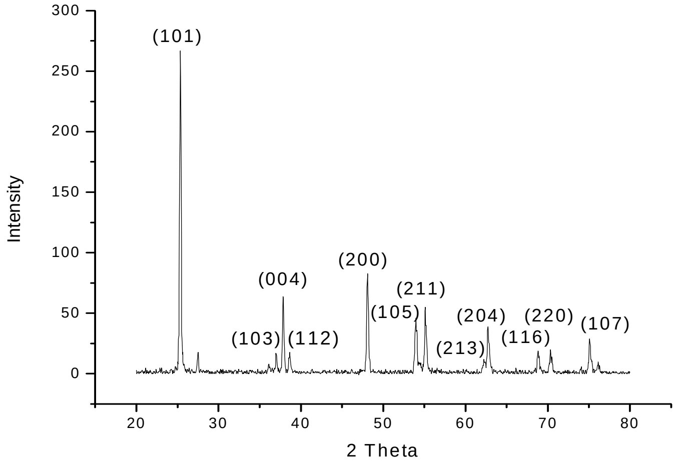


Figure 4.7: XRD Results of Al_2O_3

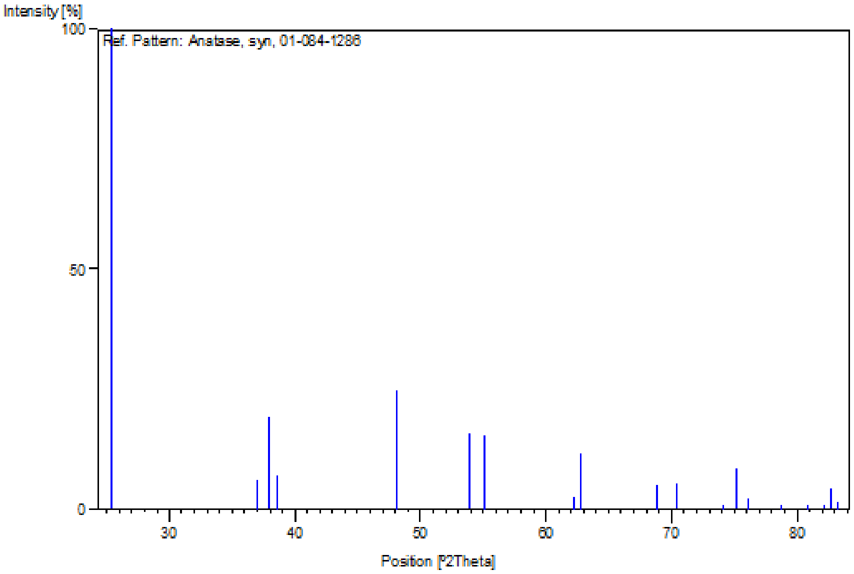


Figure 4.8: Al_2O_3Nano Particles Peak Matching with Stick Pattern

4.7.3. PSA Result of Al_2O_3 Bulk Particles

In order to analyze the particle size of this compound result at Figure 4.9 was obtained.

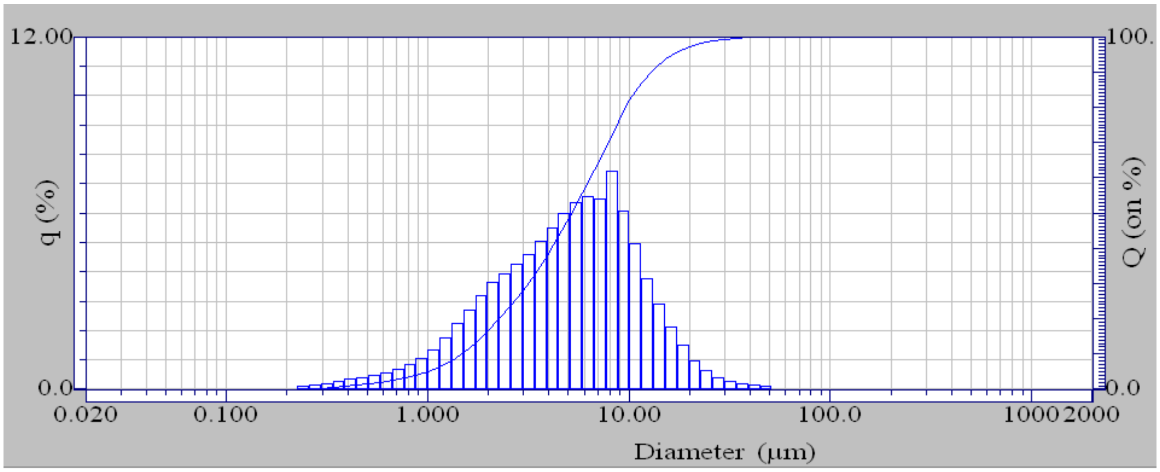


Figure 4.9: PSA Al_2O_3 Bulk (Average Particle size -10.09 µm)

Chapter 5: Results and Discussions

5. In this part results obtained by the addition of catalyst will be discussed. Comparison of the results will be carried on the basis of their physical condition and their geometry.

5.1. **Samples**

Naphtha samples were prepared and were made to undergo different cracking conditions e.g. normal room temperature (with varying stay period, 0, 2, 4, 5 hours), under UV light for 30 minutes, steam thermal cracking with different temperatures (with and without catalysts), under solar light for 20 hours. A wide range of catalyst were applied to observe the cracking, few results of the catalysts are discussed here. Results discussed here are of cracking carried under sun light and which were analyzed in the GCMS. Samples which were fed into GCMS for the cracking analysis are tabulated in Table: 5.1 basing on their physical state. There are few places in the table below where no gas found in the balloon so those places are kept empty.

Table 5.1: Sample State

S/No	Catalysts	Amount	Physical State	Physical State
1.	Naphtha(Pentane, Hexane and Heptane) Standard	40 ml sample/ 100 mg catalyst	Liquid	-
2.	Naphtha(Hexane and Heptane) Standard	20 ml sample/ 100 mg catalyst	Liquid	-
3.	CuO Bulk	40 ml/100 mg	Liquid	Gas
4.	CuO Nano Particles	40 ml/100 mg	Liquid	Gas
5.	CuO Bulk	20 ml/100 mg	Liquid	Gas

6.	CuO Nano Particles	20 ml/100 mg	Liquid	Gas
7.	Al_2O_3 Bulk	40 ml/100 mg	Liquid	-
8.	Al_2O_3Nano Particles	40 ml/100 mg	Liquid	Gas
9.	Al_2O_3 Bulk	20 ml/100 mg	Liquid	Gas
10.	Al_2O_3 Nano Particles	20 ml/100 mg	Liquid	Gas
11.	Fe_2O_3 Bulk	40 ml/100 mg	Liquid	-
12.	Fe_2O_3 Nano Particles	40 ml/100 mg	Liquid	Gas

5.2. GCMS Analysis

All GCMS results are given (Table 5.2) for reference.

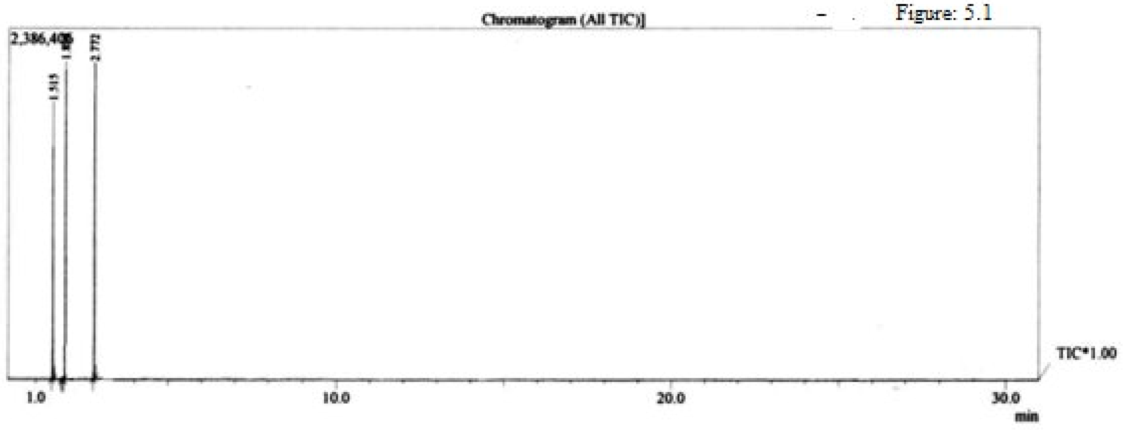
Table 5.2: GCMS Analysis

S/No	**Catalysts**	**Qty**	**Remarks**
1.	Naphtha(Pentane, Hexane and Heptane) Standard (Liquid)	40 ml sample/ 100 mg catalyst	Figure: 5.1
2.	Naphtha(Hexane and Heptane) Standard (Liquid)	20 ml sample/ 100 mg catalyst	Figure: 5.2
3.	CuO Bulk (Liquid)	40 ml/100 mg	Figure: 5.3
4.	CuO Bulk (Gas)	40 ml/100 mg	Figure: 5.4
5.	CuO Nano Particles (Liquid)	40 ml/100 mg	Figure: 5.5
6.	CuO Nano Particles (Gas)	40 ml/100 mg	Figure: 5.6
7.	CuO Bulk (Liquid)	20 ml/100 mg	Figure: 5.7
8.	CuO Bulk (Gas)	20 ml/100 mg	Figure: 5.8
9.	CuO Nano Particles(Liquid)	20 ml/100 mg	Figure: 5.9
10.	CuO Nano Particles(Gas)	20 ml/100 mg	Figure: 5.10
11.	Al_2O_3Bulk(Liquid)	40 ml/100 mg	Figure: 5.11
12.	Al_2O_3Nano Particles (Liquid)	40 ml/100 mg	Figure: 5.12
13.	Al_2O_3Nano Particles(Gas)	40 ml/100 mg	Figure: 5.13
14.	Al_2O_3 Bulk(Liquid)	20 ml/100 mg	Figure: 5.14
15.	Al_2O_3 Bulk(Gas)	20 ml/100 mg	Figure: 5.15

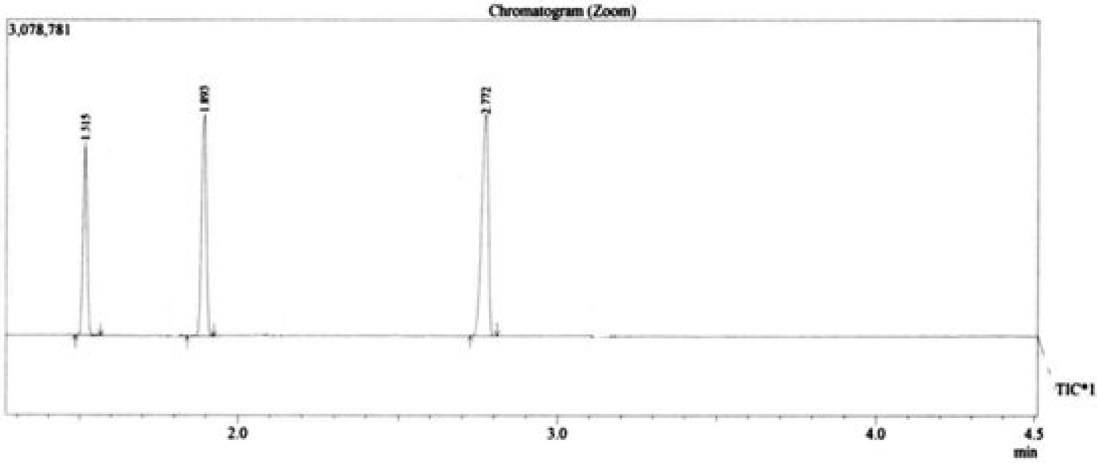
16.	Al_2O_3 Nano Particles(Liquid)	20 ml/100 mg	Figure: 5.16
17.	Al_2O_3 Nano Particles(Gas)	20 ml/100 mg	Figure: 5.17
18.	Fe_2O_3Bulk (Liquid)	40 ml/100 mg	Figure: 5.18
19.	Fe_2O_3 Nano Particles (Liquid)	40 ml/100 mg	Figure: 5.19
20.	Fe_2O_3 Nano Particles (Gas)	40 ml/100 mg	Figure: 5.20

Figure: 5.1

Chromatogram (All TIC)]



Chromatogram (Zoom)



Spectrum

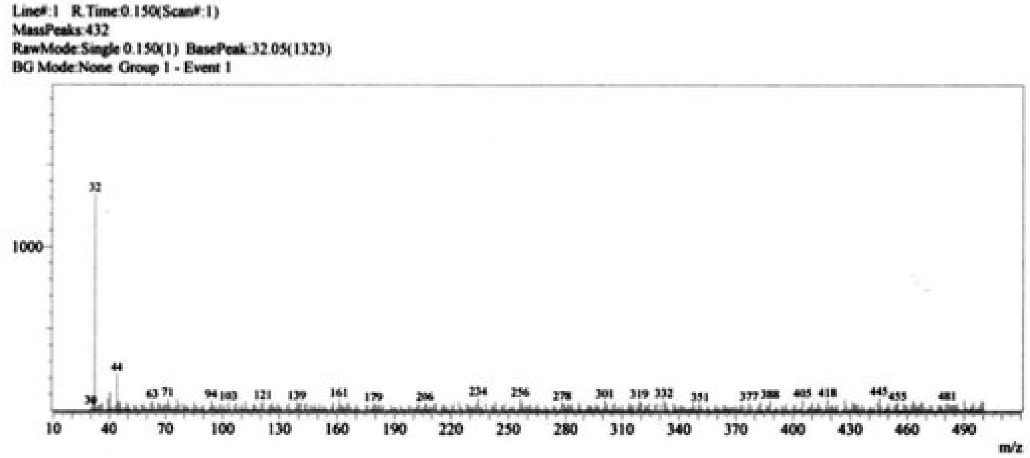


Figure 5.2

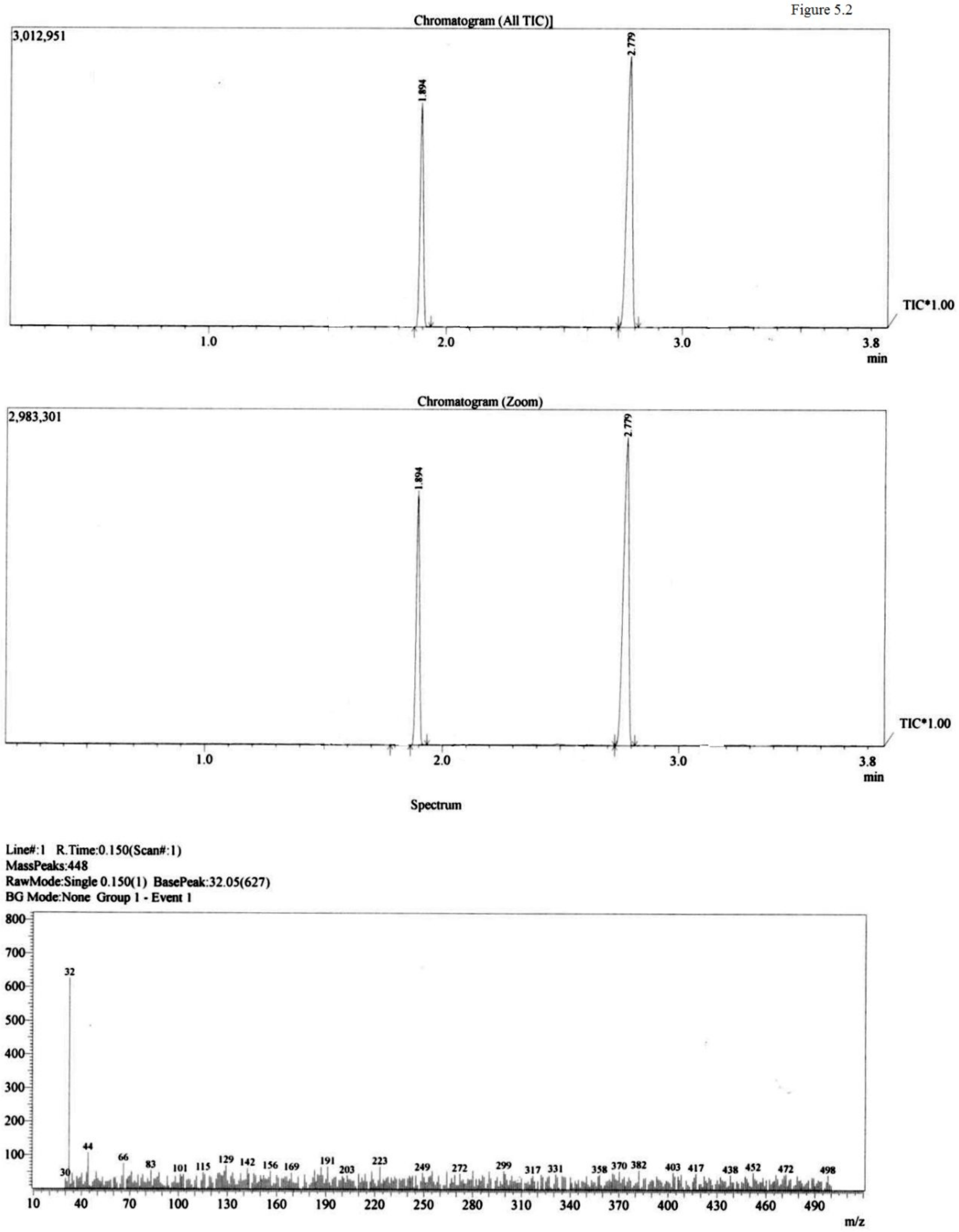

Chromatogram (All TIC)]
3,012,951
1.894
2.779
TIC*1.00
1.0
2.0
3.0
3.8
min
Chromatogram (Zoom)
2,983,301
1.894
2.779
TIC*1.00
1.0
2.0
3.0
3.8
min
Spectrum
Line#:1 R.Time:0.150(Scan#:1)
MassPeaks:448
RawMode:Single 0.150(1) BasePeak:32.05(627)
BG Mode:None Group 1 - Event 1
800
700
600
500
400
300
200
100
32
30
44
66
83
101
115
129
142
156
169
191
203
223
249
272
299
317
331
358
370
382
403
417
438
452
472
498
10
40
70
100
130
160
190
220
250
280
310
340
370
400
430
460
490
m/z

Figure: 5.3

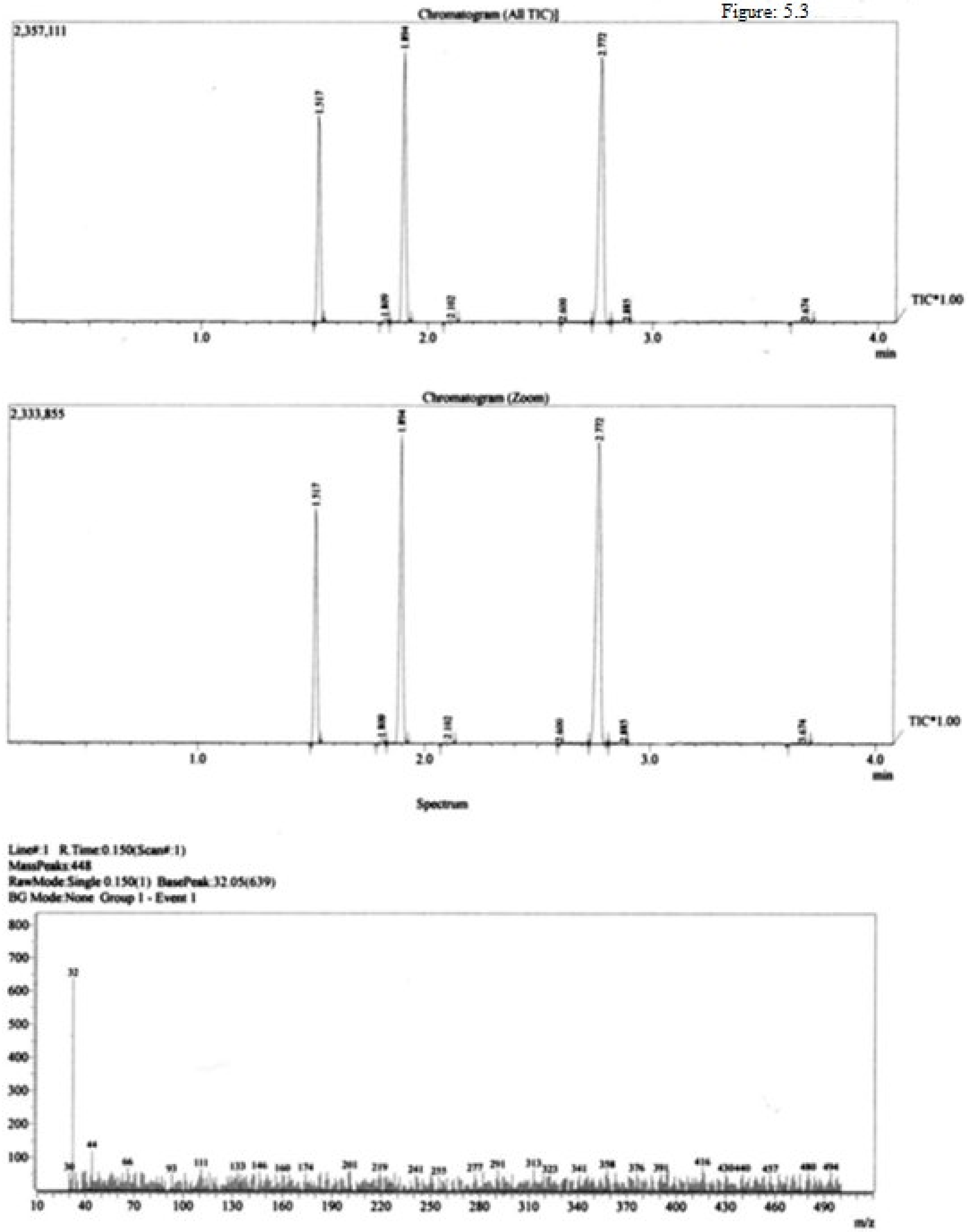

Chromatogram (All TIC)]
2,357,111
1.517
1.894
2.772
1.809
2.102
2.600
2.883
3.674
TIC*1.00
1.0
2.0
3.0
4.0
min
Chromatogram (Zoom)
2,333,855
1.517
1.894
2.772
1.809
2.102
2.600
2.883
3.674
TIC*1.00
1.0
2.0
3.0
4.0
min
Spectrum
Line#:1 R.Time:0.150(Scan#:1)
MassPeaks:448
RawMode:Single 0.150(1) BasePeak:32.05(639)
BG Mode:None Group 1 - Event 1
800
700
600
500
400
300
200
100
32
44
30
66
93
111
133
146
160
174
201
219
241
255
277
291
313
323
341
358
376
391
416
430440
457
480
494
10
40
70
100
130
160
190
220
250
280
310
340
370
400
430
460
490
m/z

Figure: 5.4

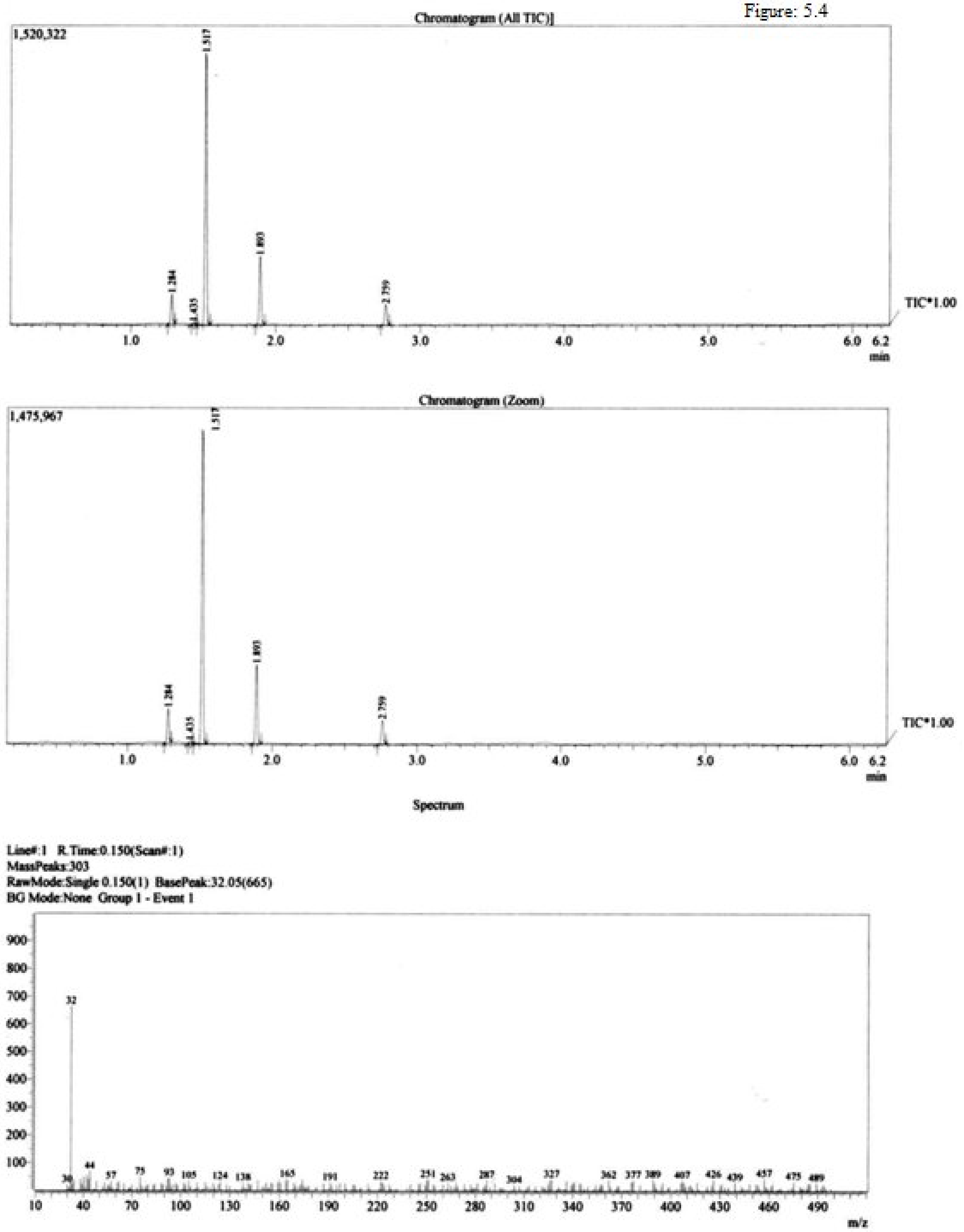

Chromatogram (All TIC)]
1,520,322
1.284
1.435
1.517
1.893
2.759
TIC*1.00
1.0
2.0
3.0
4.0
5.0
6.0 6.2
min
Chromatogram (Zoom)
1,475,967
1.284
1.435
1.517
1.893
2.759
TIC*1.00
1.0
2.0
3.0
4.0
5.0
6.0 6.2
min
Spectrum
Line#:1 R.Time:0.150(Scan#:1)
MassPeaks:303
RawMode:Single 0.150(1) BasePeak:32.05(665)
BG Mode:None Group 1 - Event 1
900
800
700
600
500
400
300
200
100
32
30
44
57
75
93
105
124
138
165
191
222
251
263
287
304
327
362
377
389
407
426
439
457
475
489
10
40
70
100
130
160
190
220
250
280
310
340
370
400
430
460
490
m/z

Figure: 5.5

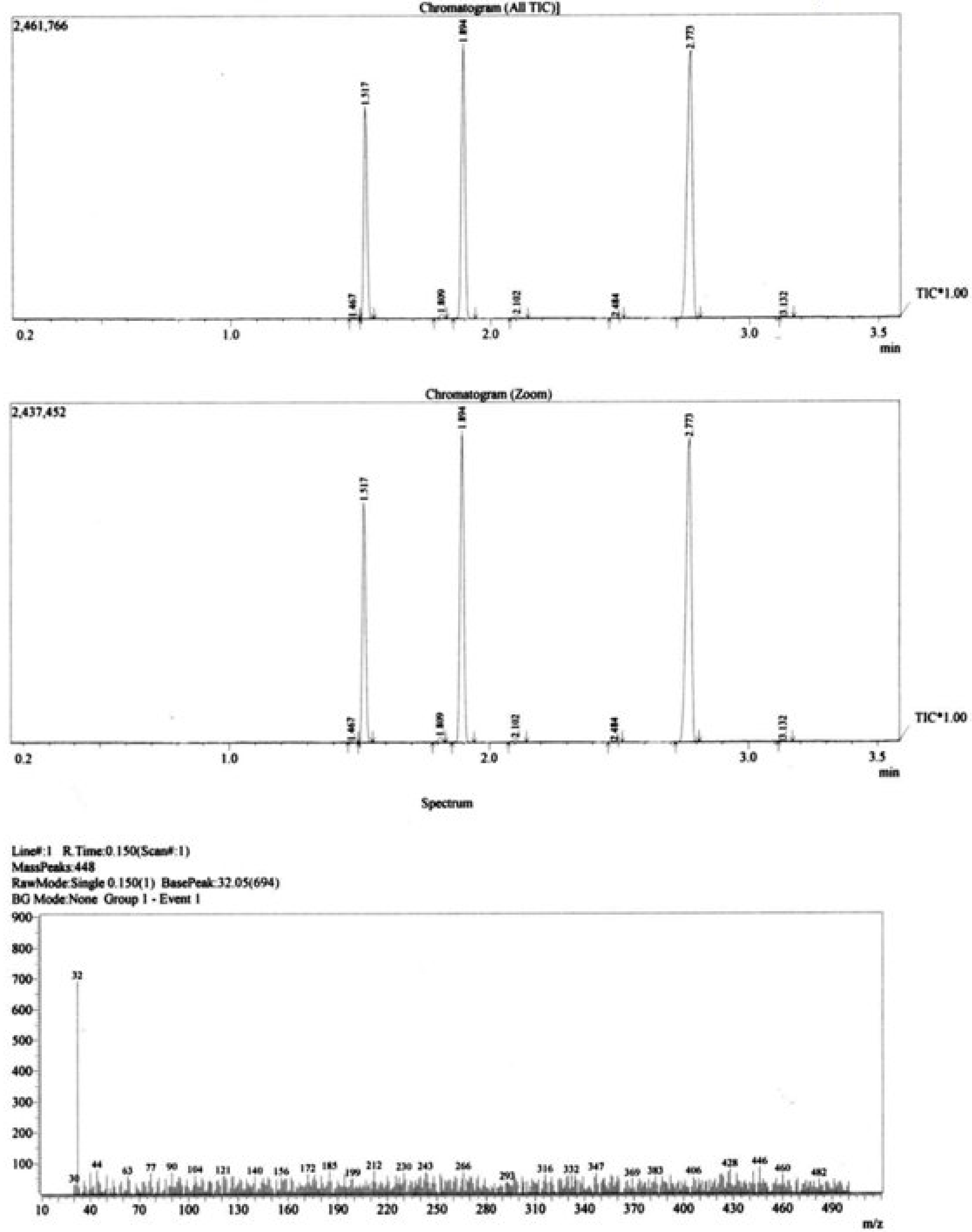
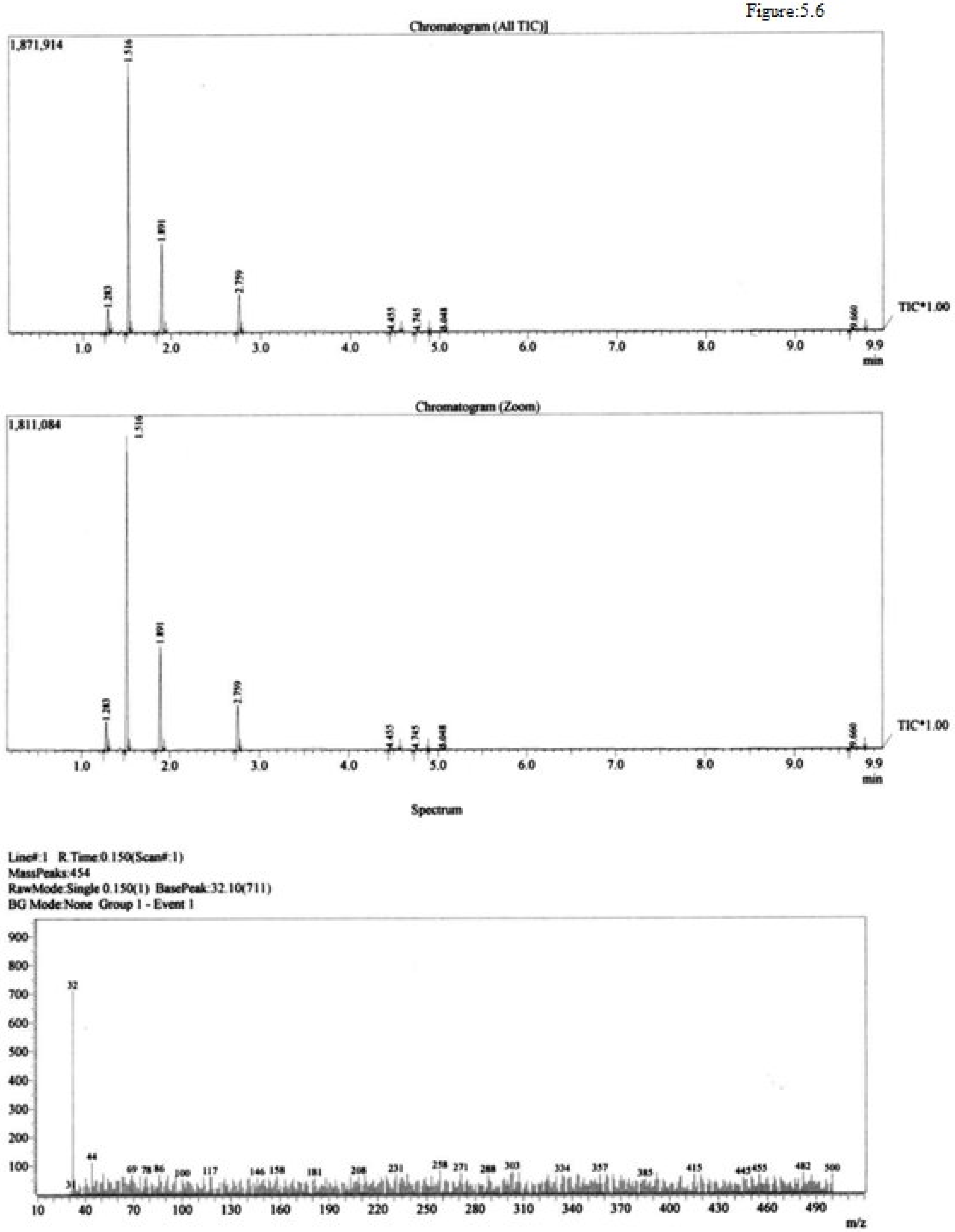

Chromatogram (All TIC)]
2,461,766
1.467
1.517
1.809
1.894
2.102
2.484
2.773
3.132
TIC*1.00
0.2
1.0
2.0
3.0
3.5
min
Chromatogram (Zoom)
2,437,452
1.467
1.517
1.809
1.894
2.102
2.484
2.773
3.132
TIC*1.00
0.2
1.0
2.0
3.0
3.5
min
Spectrum
Line#:1 R.Time:0.150(Scan#:1)
MassPeaks:448
RawMode:Single 0.150(1) BasePeak:32.05(694)
BG Mode:None Group 1 - Event 1
900
800
700
600
500
400
300
200
100
32
30
44
63
77
90
104
121
140
156
172
185
199
212
230
243
266
293
316
332
347
369
383
406
428
446
460
482
10
40
70
100
130
160
190
220
250
280
310
340
370
400
430
460
490
m/z

Figure:5.6



```
Line#:1   R.Time:0.150(Scan#:1)
MassPeaks:454
RawMode:Single 0.150(1)  BasePeak:32.10(711)
BG Mode:None  Group 1 - Event 1
```

Figure: 5.7

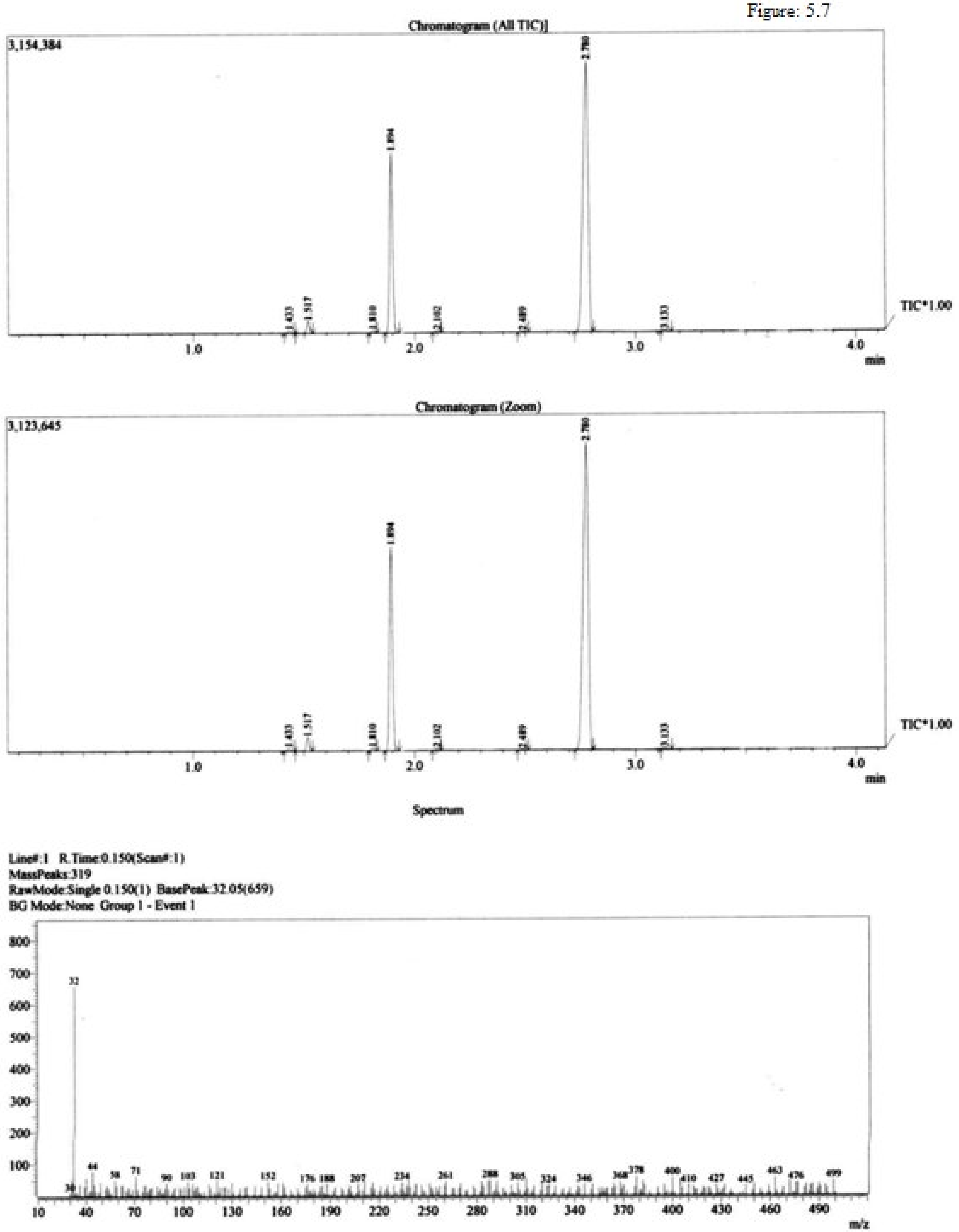

Chromatogram (All TIC)]
3,154,384
1.433
1.517
1.810
1.894
2.102
2.489
2.780
3.133
TIC*1.00
1.0
2.0
3.0
4.0
min
Chromatogram (Zoom)
3,123,645
1.433
1.517
1.810
1.894
2.102
2.489
2.780
3.133
TIC*1.00
1.0
2.0
3.0
4.0
min
Spectrum
Line#:1 R.Time:0.150(Scan#:1)
MassPeaks:319
RawMode:Single 0.150(1) BasePeak:32.05(659)
BG Mode:None Group 1 - Event 1
800
700
600
500
400
300
200
100
32
30
44
58
71
90
103
121
152
176
188
207
234
261
288
305
324
346
368
378
400
410
427
445
463
476
499
10
40
70
100
130
160
190
220
250
280
310
340
370
400
430
460
490
m/z

Figure: 5.8

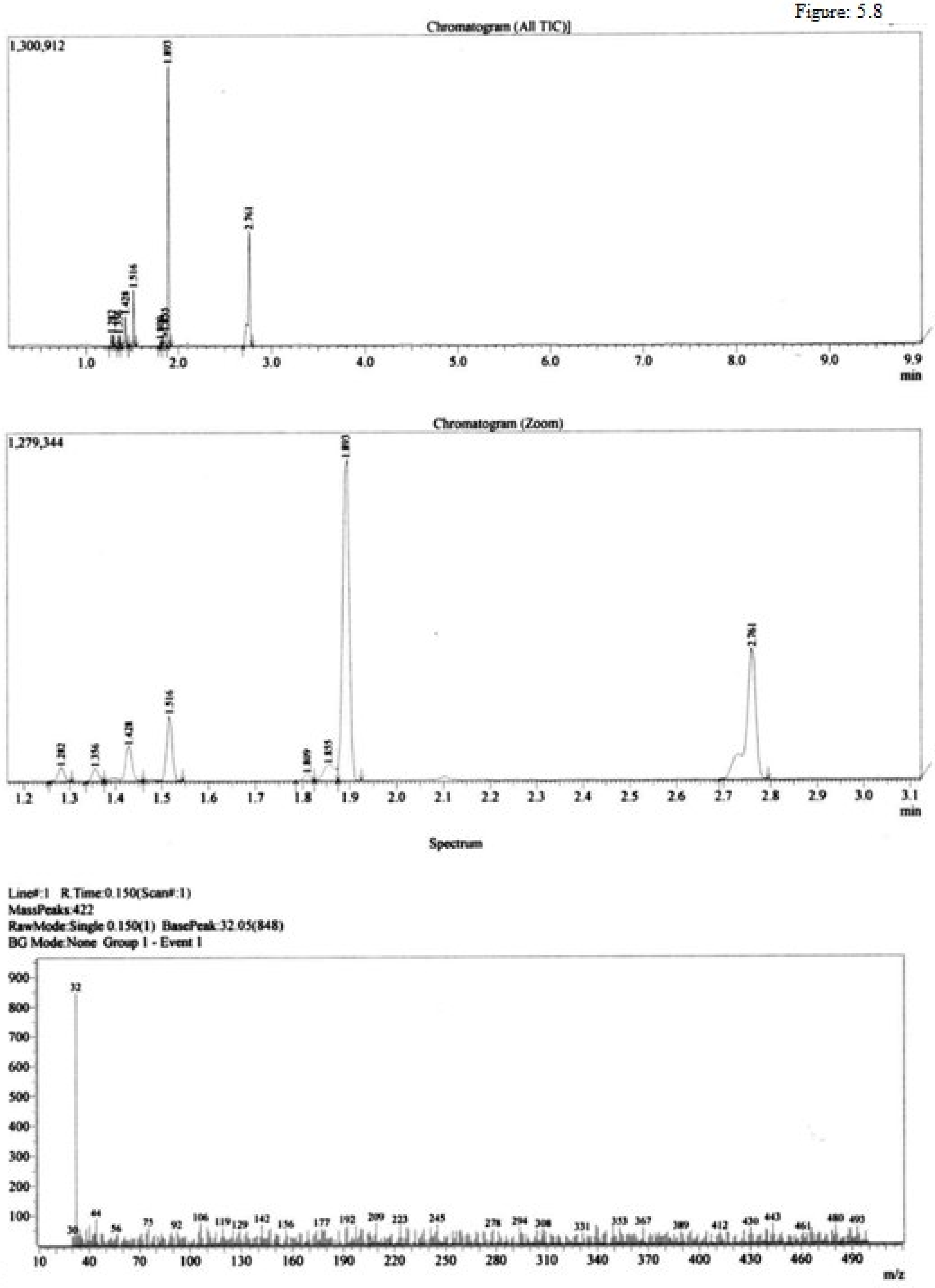
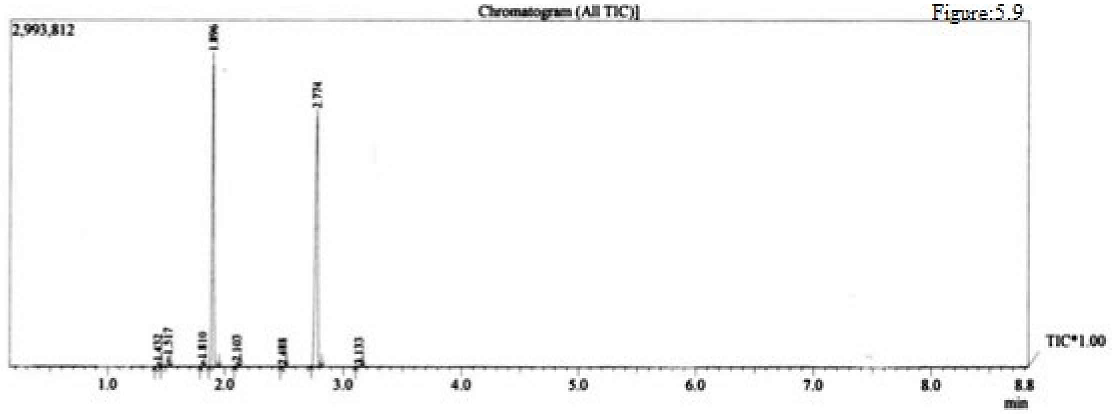
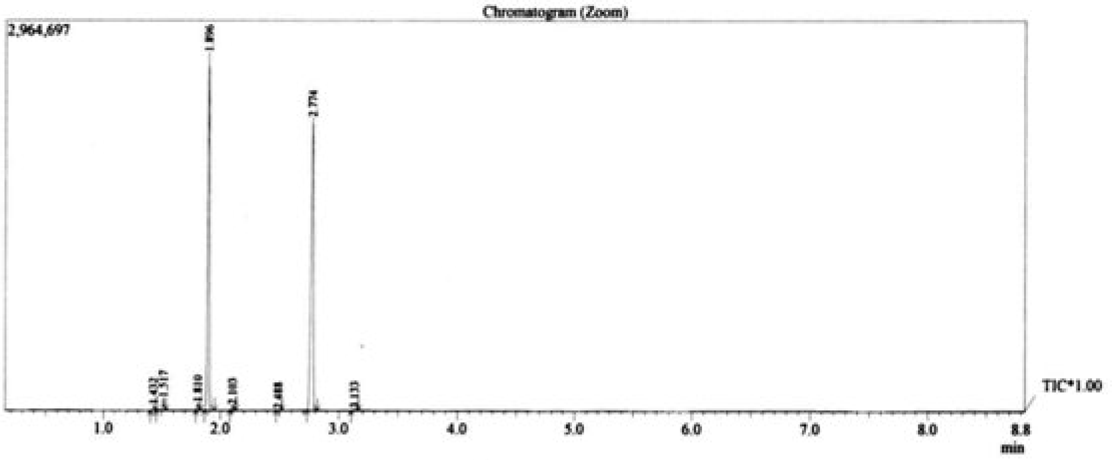

Chromatogram (All TIC)]
1,300,912
1.893
2.761
1.516
1.428
TIC*1.00
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
9.9
min
Chromatogram (Zoom)
1,279,344
1.893
2.761
1.516
1.428
1.282
1.356
1.809
1.855
TIC*1.00
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3.0
3.1
min
Spectrum
Line#:1 R.Time:0.150(Scan#:1)
MassPeaks:422
RawMode:Single 0.150(1) BasePeak:32.05(848)
BG Mode:None Group 1 - Event 1
900
800
700
600
500
400
300
200
100
32
30
44
56
75
92
106
119
129
142
156
177
192
209
223
245
278
294
308
331
353
367
389
412
430
443
461
480
493
10
40
70
100
130
160
190
220
250
280
310
340
370
400
430
460
490
m/z

Figure:5.9


Chromatogram (All TIC)]


Chromatogram (Zoom)

Spectrum

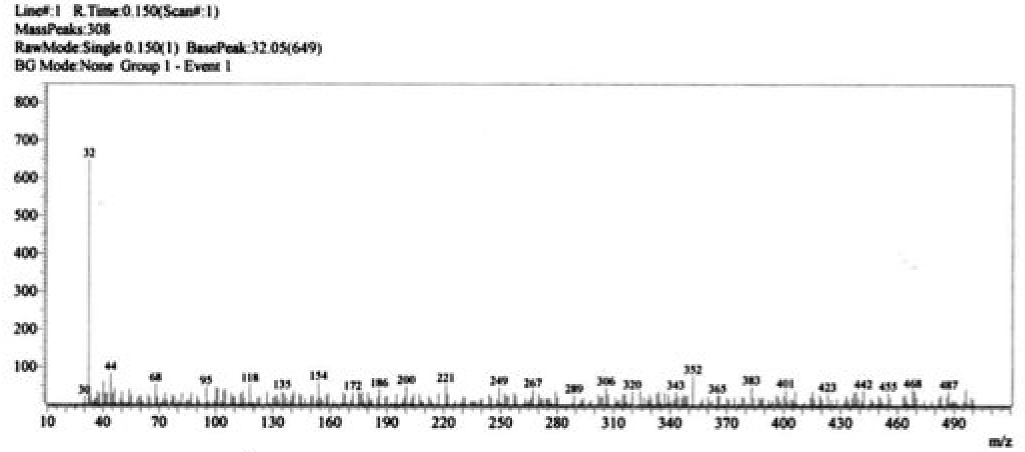
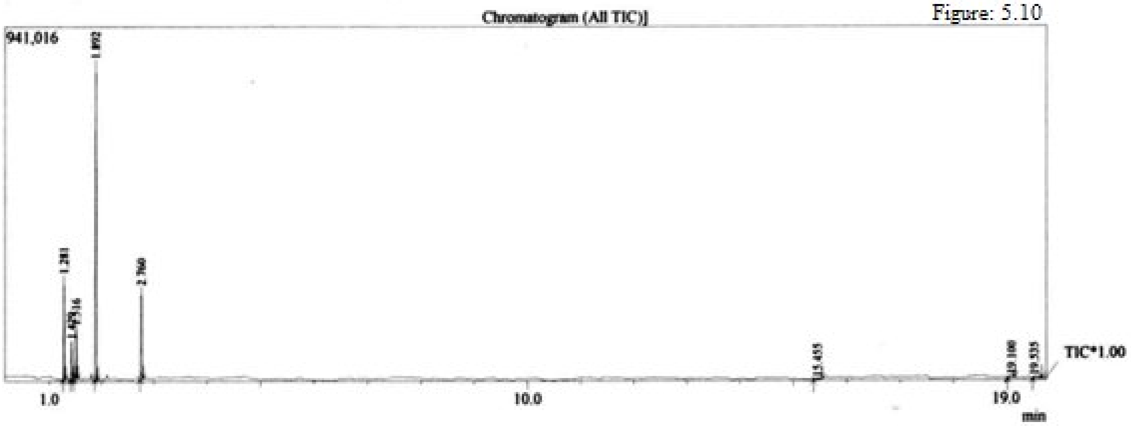
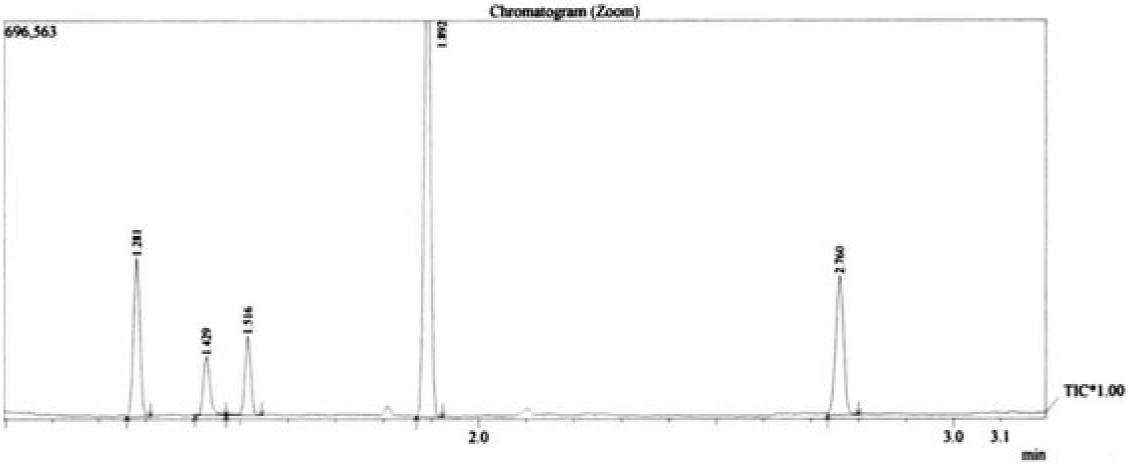


Figure: 5.10

Chromatogram (All TIC)]



Chromatogram (Zoom)



Spectrum

Line#:1 R.Time:1.280(Scan#:227)
MassPeaks:421
RawMode:Single 1.280(227) BasePeak:32.10(254820)
BG Mode:None Group 1 - Event 1

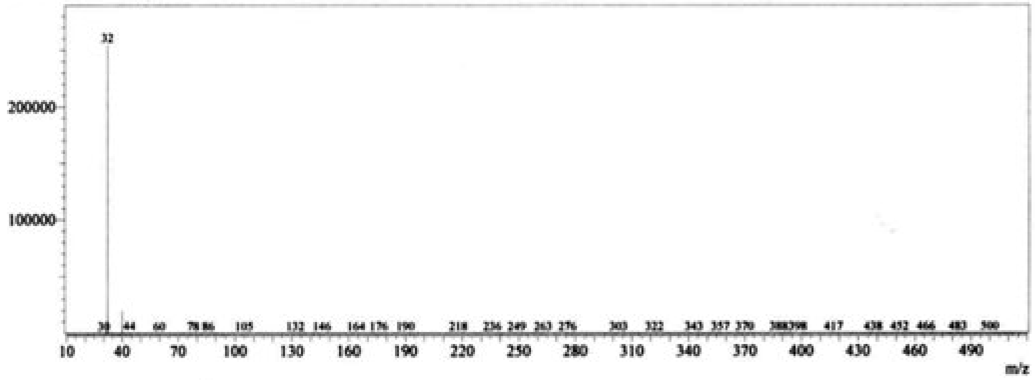


Figure: 5.11

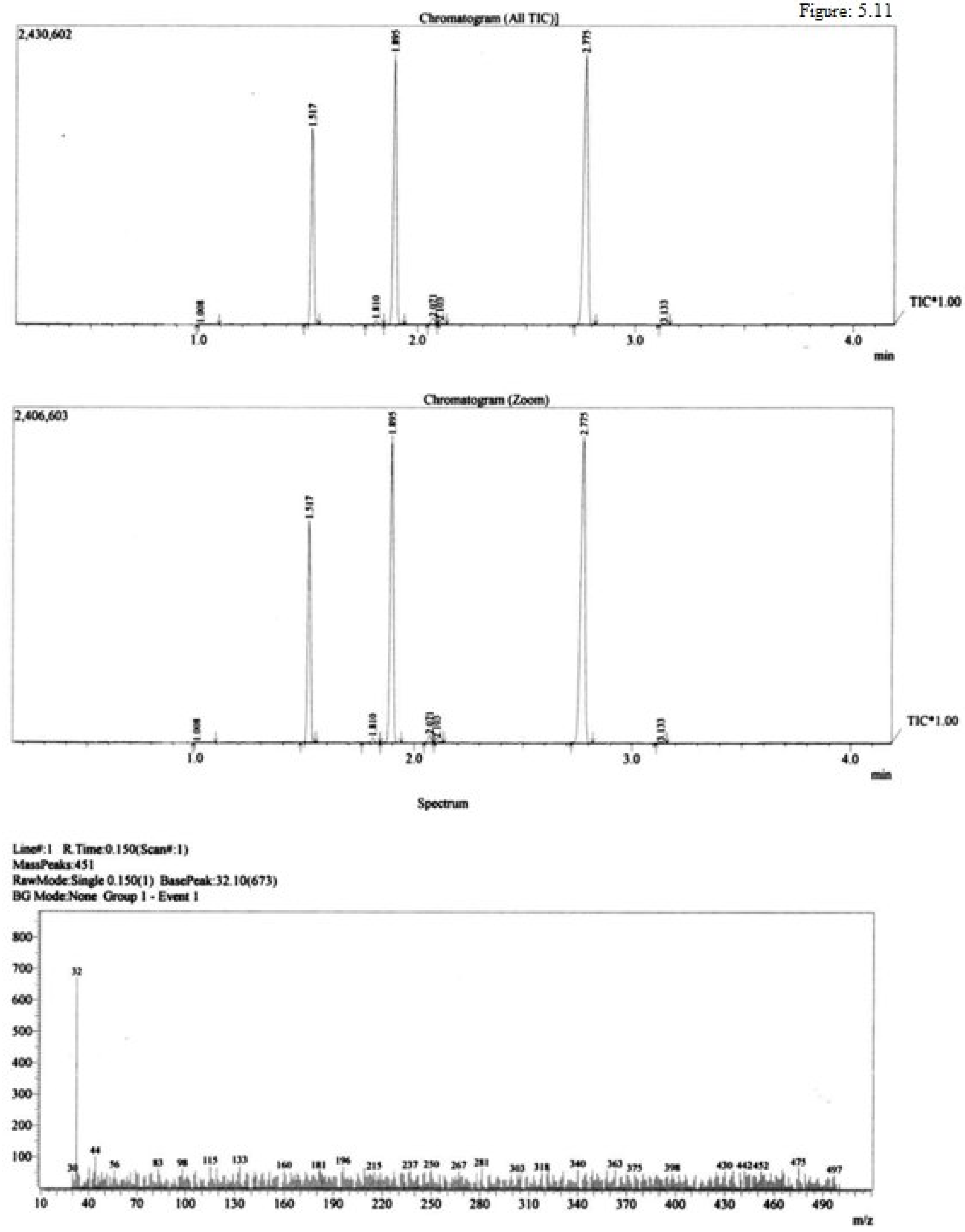

Chromatogram (All TIC)]
2,430,602
1.008
1.517
1.810
1.895
2.073
2.103
2.775
3.133
TIC*1.00
1.0
2.0
3.0
4.0
min
Chromatogram (Zoom)
2,406,603
1.008
1.517
1.810
1.895
2.073
2.103
2.775
3.133
TIC*1.00
1.0
2.0
3.0
4.0
min
Spectrum
Line#:1 R.Time:0.150(Scan#:1)
MassPeaks:451
RawMode:Single 0.150(1) BasePeak:32.10(673)
BG Mode:None Group 1 - Event 1
800
700
600
500
400
300
200
100
32
30
44
56
83
98
115
133
160
181
196
215
237
250
267
281
303
318
340
363
375
398
430
442
452
475
497
10
40
70
100
130
160
190
220
250
280
310
340
370
400
430
460
490
m/z

Figure:5.12

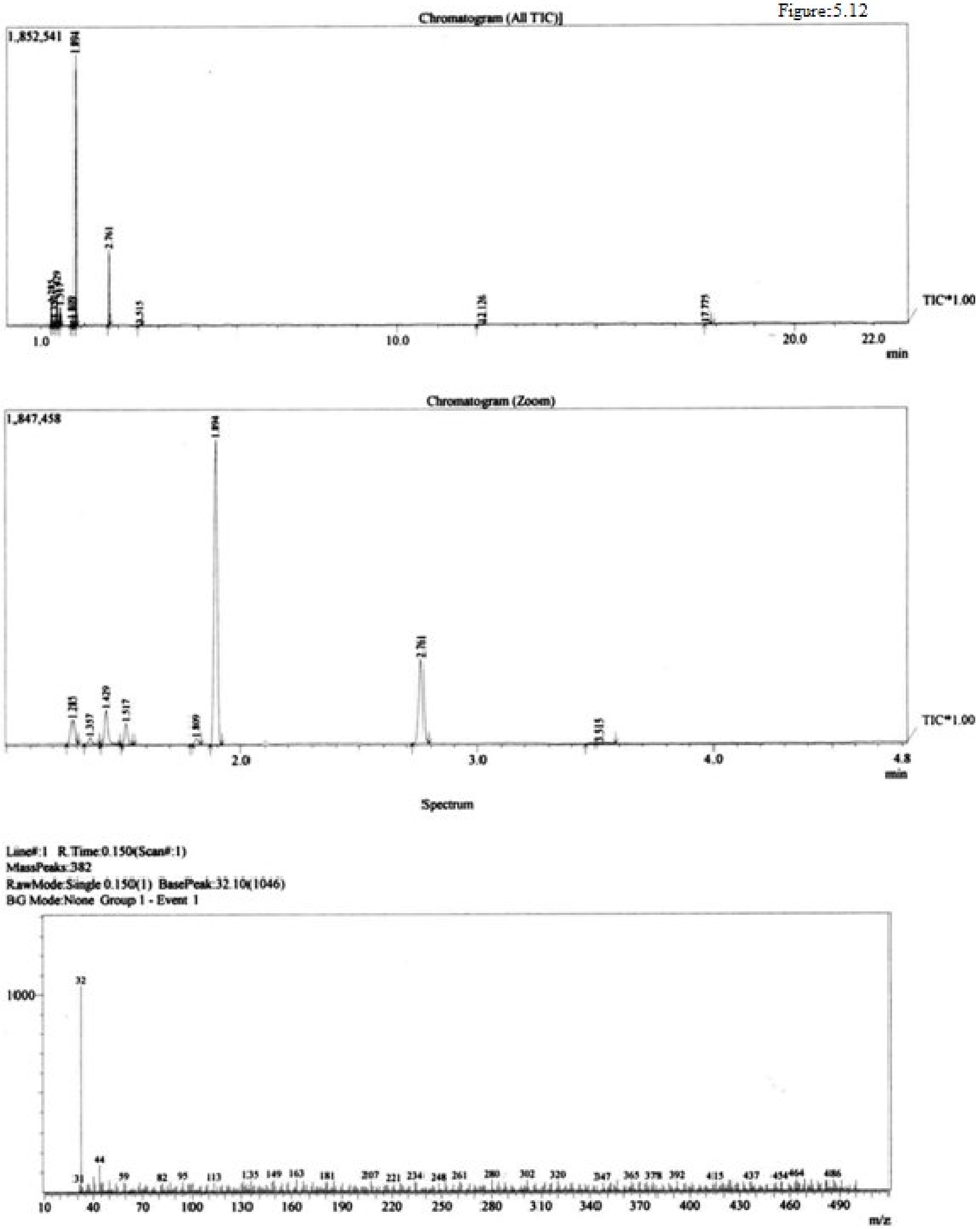
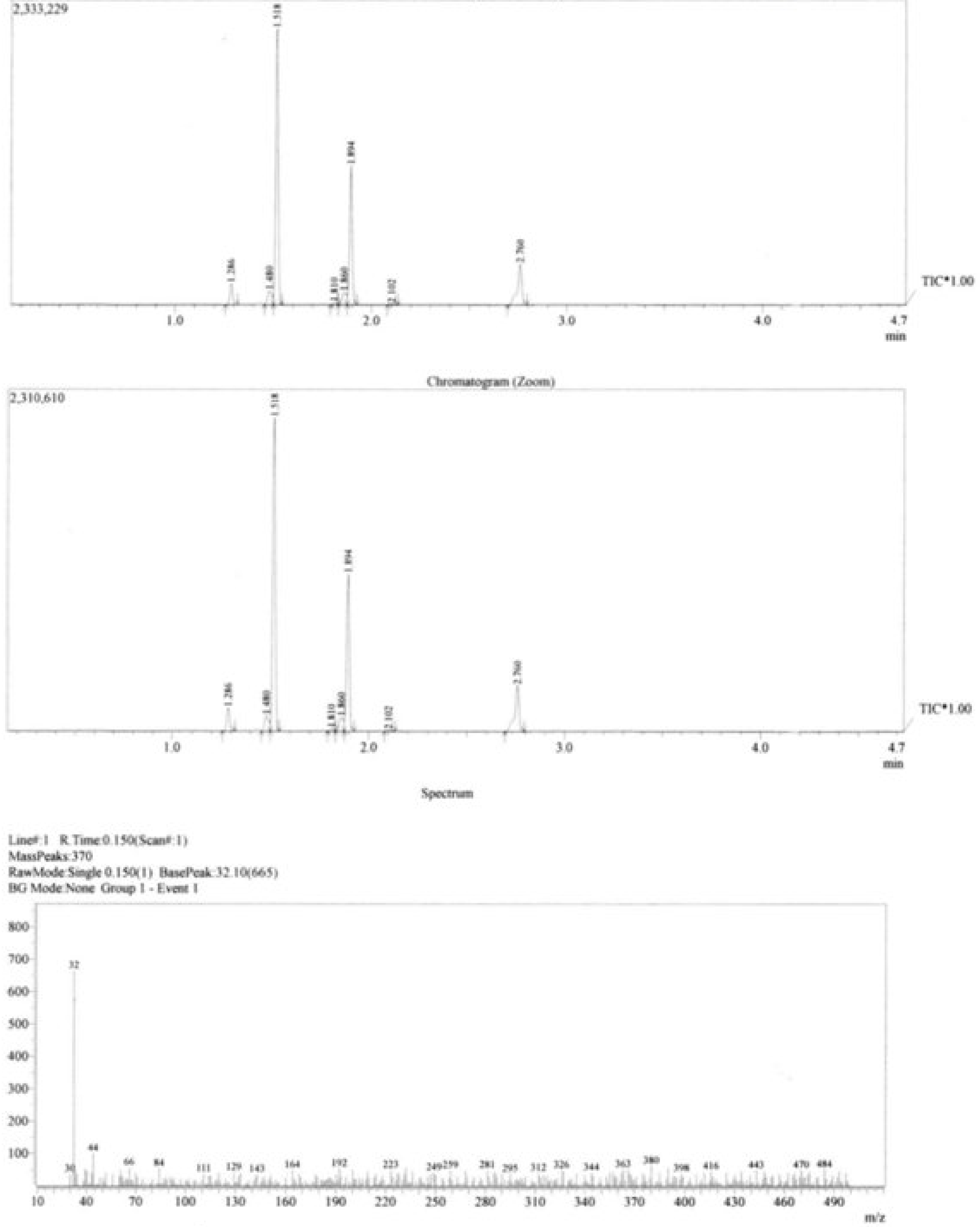

Chromatogram (All TIC)]
1,852,541
1.894
2.761
3.515
12.126
17.775
TIC*1.00
1.0
10.0
20.0
22.0
min
Chromatogram (Zoom)
1,847,458
1.894
2.761
1.283
1.337
1.429
1.517
1.809
3.515
TIC*1.00
2.0
3.0
4.0
4.8
min
Spectrum
Line#:1 R.Time:0.150(Scan#:1)
MassPeaks:382
RawMode:Single 0.150(1) BasePeak:32.10(1046)
BG Mode:None Group 1 - Event 1
1000
32
31
44
59
82
95
113
135
149
163
181
207
221
234
248
261
280
302
320
347
365
378
392
415
437
454
464
486
10
40
70
100
130
160
190
220
250
280
310
340
370
400
430
460
490
m/z

Figure: 5.13



Chromatogram (All TIC)]
2,333,229
1.286
1.480
1.518
1.810
1.860
1.894
2.102
2.760
TIC*1.00
1.0
2.0
3.0
4.0
4.7
min
Chromatogram (Zoom)
2,310,610
1.286
1.480
1.518
1.810
1.860
1.894
2.102
2.760
TIC*1.00
1.0
2.0
3.0
4.0
4.7
min
Spectrum
Line#:1 R.Time:0.150(Scan#:1)
MassPeaks:370
RawMode:Single 0.150(1) BasePeak:32.10(665)
BG Mode:None Group 1 - Event 1
800
700
600
500
400
300
200
100
32
30
44
66
84
111
129
143
164
192
223
249
259
281
295
312
326
344
363
380
398
416
443
470
484
10
40
70
100
130
160
190
220
250
280
310
340
370
400
430
460
490
m/z

Figure: 5.14

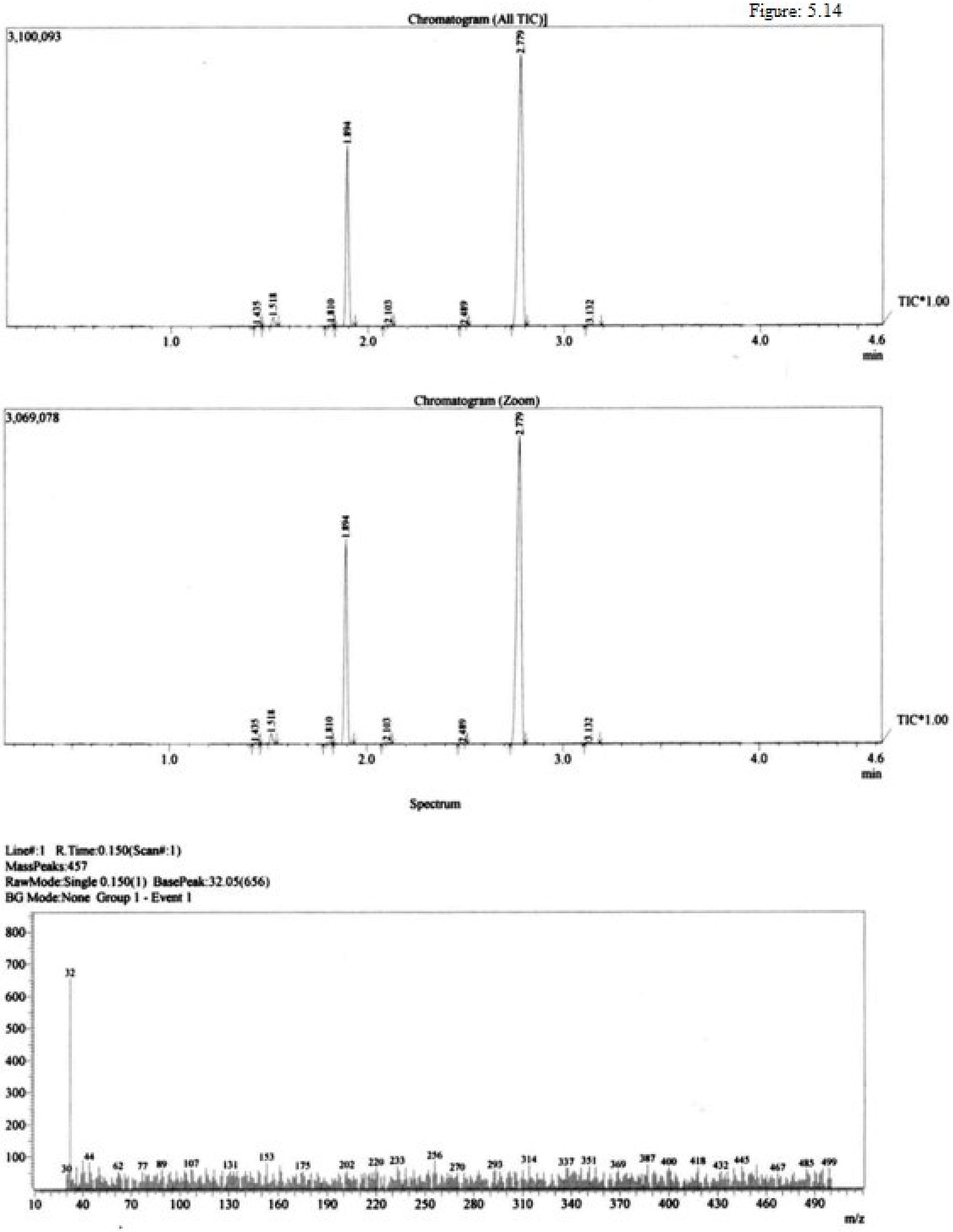

Chromatogram (All TIC)]
3,100,093
1.435
1.518
1.810
1.894
2.103
2.489
2.779
3.132
TIC*1.00
1.0
2.0
3.0
4.0
4.6
min
Chromatogram (Zoom)
3,069,078
1.435
1.518
1.810
1.894
2.103
2.489
2.779
3.132
TIC*1.00
1.0
2.0
3.0
4.0
4.6
min
Spectrum
Line#:1 R.Time:0.150(Scan#:1)
MassPeaks:457
RawMode:Single 0.150(1) BasePeak:32.05(656)
BG Mode:None Group 1 - Event 1
800
700
600
500
400
300
200
100
32
30
44
62
77
89
107
131
153
175
202
220
233
256
270
293
314
337
351
369
387
400
418
432
445
467
485
499
10
40
70
100
130
160
190
220
250
280
310
340
370
400
430
460
490
m/z

Figure: 5.15

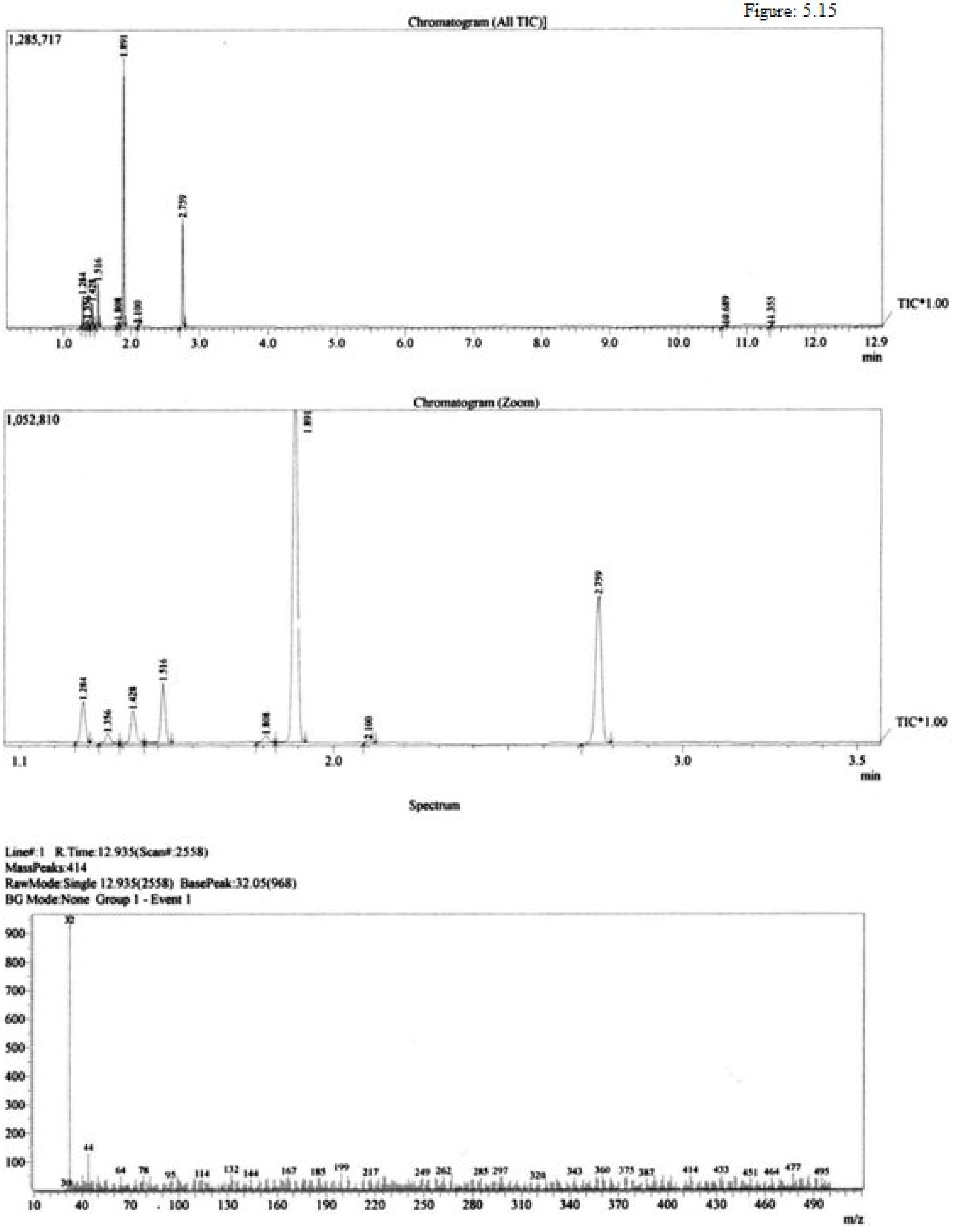

Chromatogram (All TIC)]
1,285,717
1.284
1.356
1.428
1.516
1.808
1.891
2.100
2.759
10.689
11.355
TIC*1.00
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
12.9
min
Chromatogram (Zoom)
1,052,810
1.284
1.356
1.428
1.516
1.808
1.891
2.100
2.759
TIC*1.00
1.1
2.0
3.0
3.5
min
Spectrum
Line#:1 R.Time:12.935(Scan#:2558)
MassPeaks:414
RawMode:Single 12.935(2558) BasePeak:32.05(968)
BG Mode:None Group 1 - Event 1
32
44
30
64
78
95
114
132
144
167
185
199
217
249
262
285
297
326
343
360
375
387
414
433
451
464
477
495
900
800
700
600
500
400
300
200
100
10
40
70
100
130
160
190
220
250
280
310
340
370
400
430
460
490
m/z

Figure: 5.16

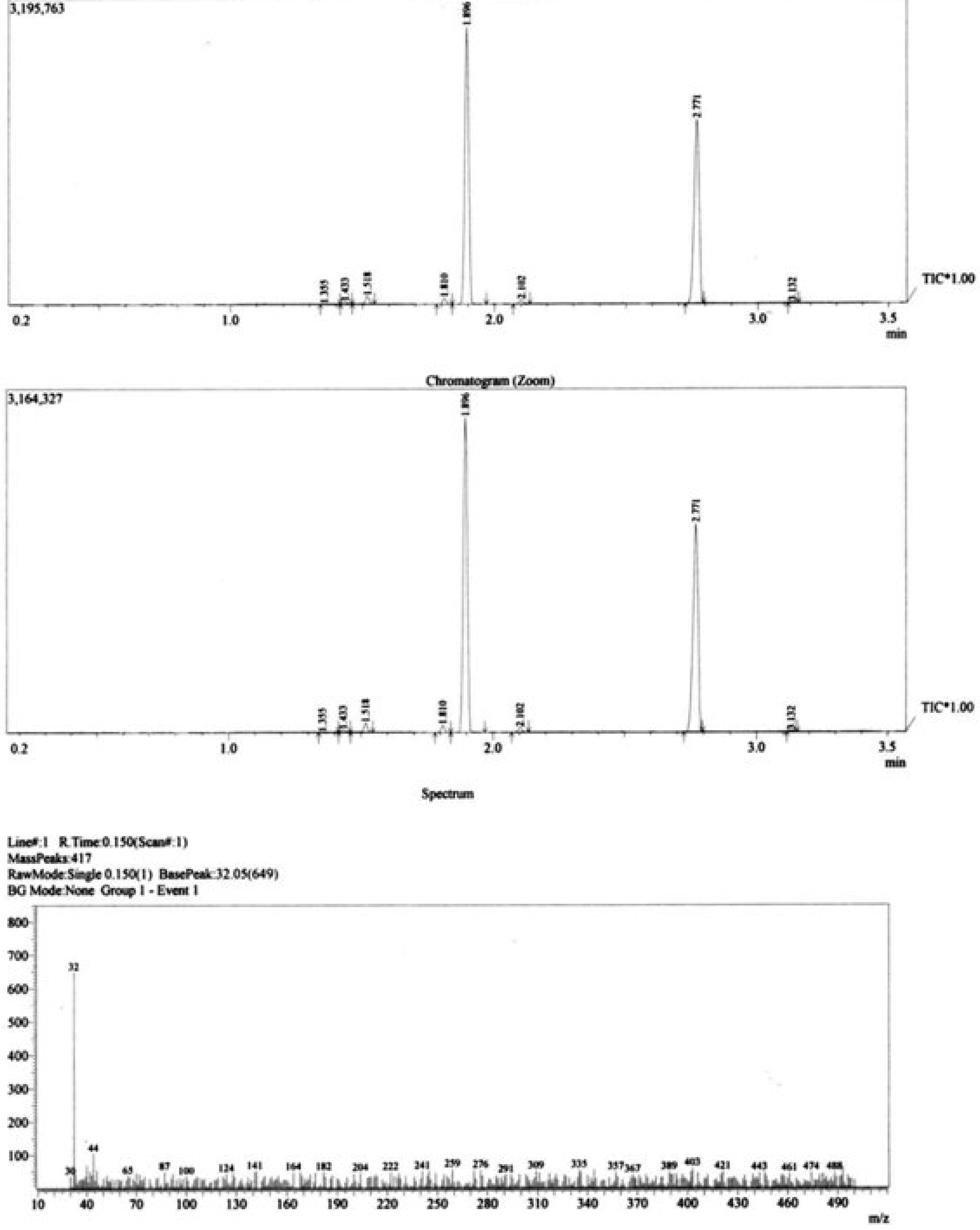
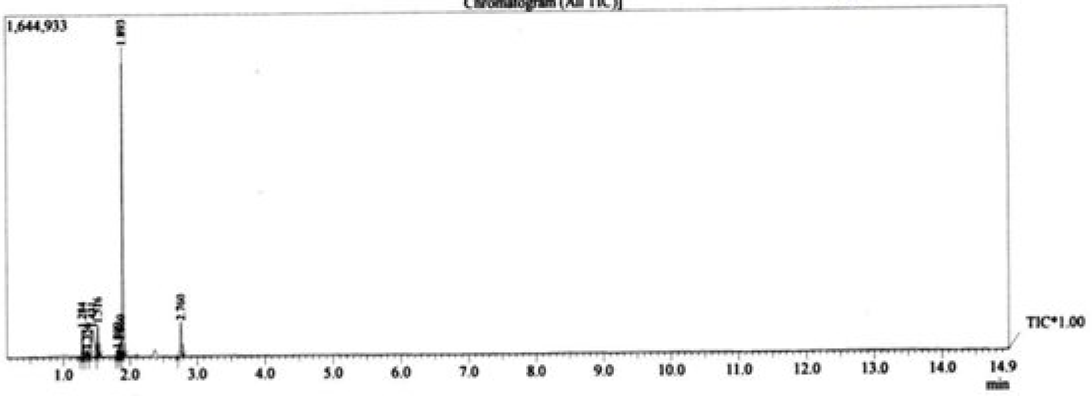
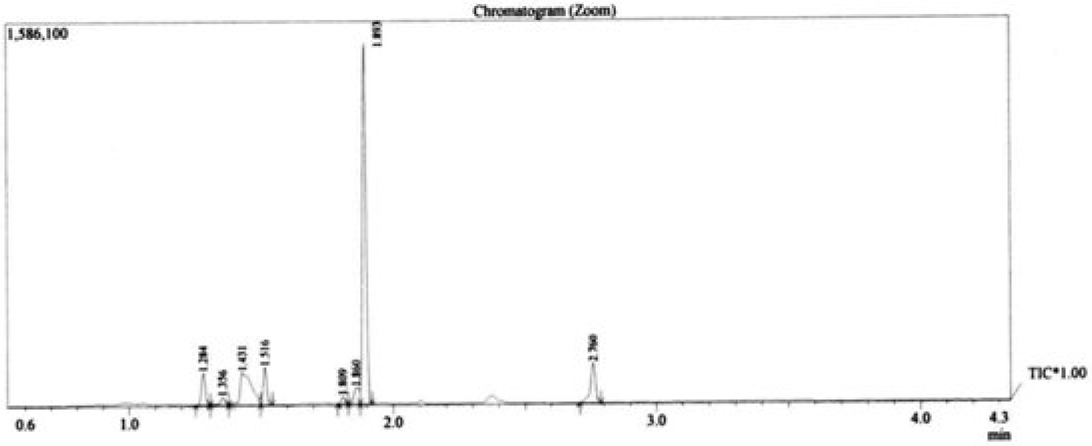

Chromatogram (All TIC)]
3,195,763
1.335
1.433
1.518
1.810
1.896
2.102
2.771
3.132
TIC*1.00
0.2
1.0
2.0
3.0
3.5
min
Chromatogram (Zoom)
3,164,327
1.335
1.433
1.518
1.810
1.896
2.102
2.771
3.132
TIC*1.00
0.2
1.0
2.0
3.0
3.5
min
Spectrum
Line#:1 R.Time:0.150(Scan#:1)
MassPeaks:417
RawMode:Single 0.150(1) BasePeak:32.05(649)
BG Mode:None Group 1 - Event 1
800
700
600
500
400
300
200
100
32
44
30
65
87
100
124
141
164
182
204
222
241
259
276
291
309
335
357
367
389
403
421
443
461
474
488
10
40
70
100
130
160
190
220
250
280
310
340
370
400
430
460
490
m/z

Figure: 5.17

Chromatogram (All TIC)]



Chromatogram (Zoom)



Spectrum

Line#:1 R.Time:1.290(Scan#:229)
MassPeaks:422
RawMode:Single 1.290(229) BasePeak:44.00(49764)
BG Mode:None Group 1 - Event 1

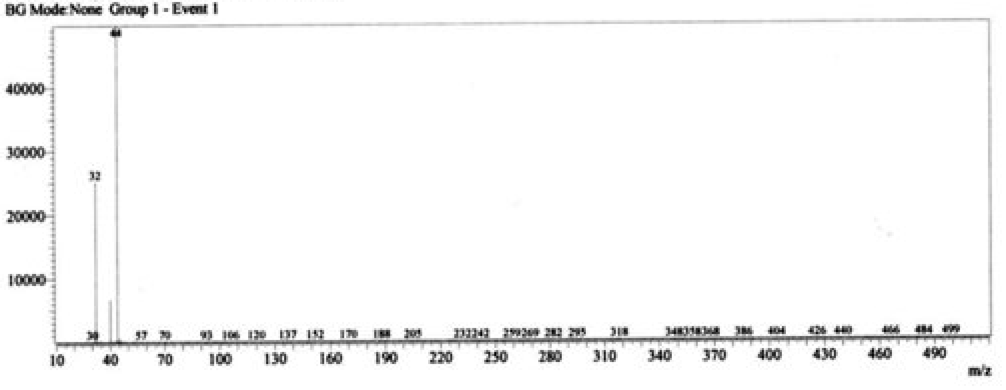
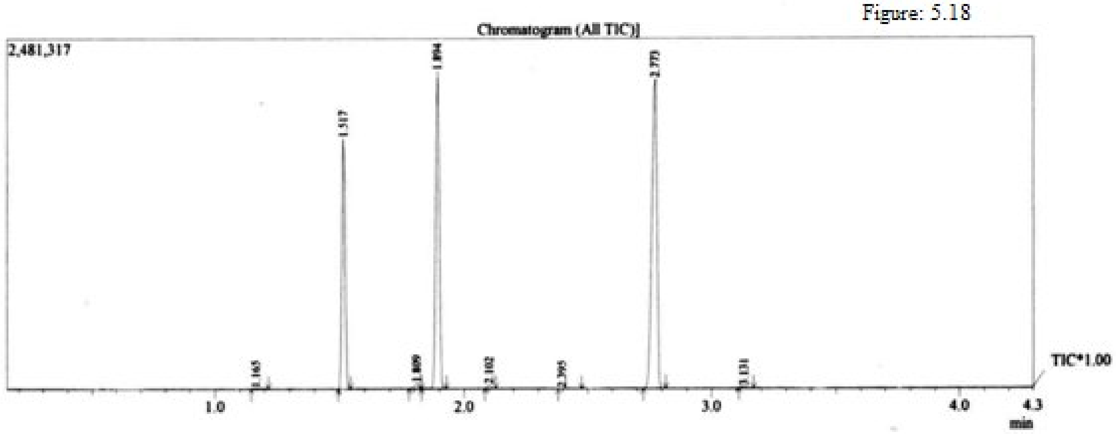
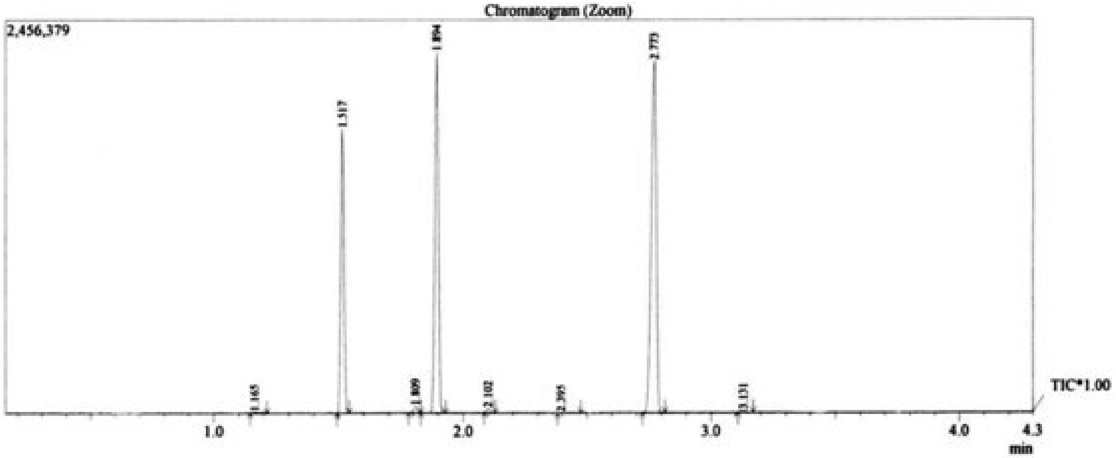


Figure: 5.18


Chromatogram (All TIC)]
2,481,317
1.165
1.517
1.809
1.894
2.102
2.395
2.773
3.131
TIC*1.00
1.0
2.0
3.0
4.0
4.3
min


Chromatogram (Zoom)
2,456,379
1.165
1.517
1.809
1.894
2.102
2.395
2.773
3.131
TIC*1.00
1.0
2.0
3.0
4.0
4.3
min

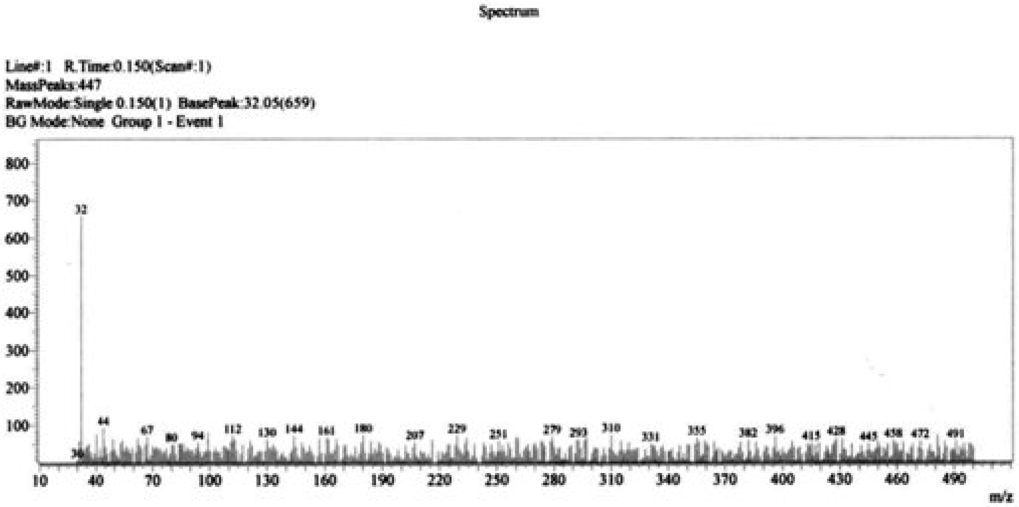
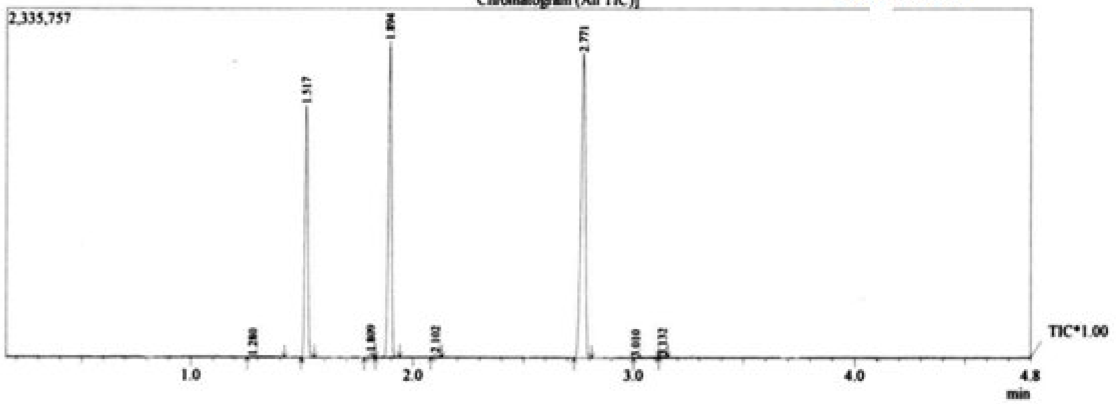
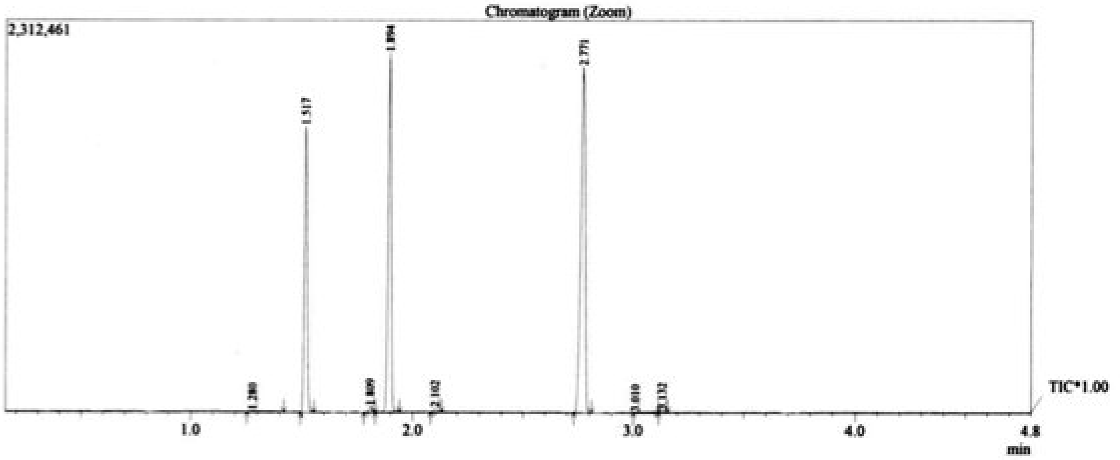

Spectrum
Line#:1 R.Time:0.150(Scan#:1)
MassPeaks:447
RawMode:Single 0.150(1) BasePeak:32.05(659)
BG Mode:None Group 1 - Event 1
800
700
600
500
400
300
200
100
32
36
44
67
80
94
112
130
144
161
180
207
229
251
279
293
310
331
355
382
396
415
428
445
458
472
491
10
40
70
100
130
160
190
220
250
280
310
340
370
400
430
460
490
m/z

Figure: 5.19

Chromatogram (All TIC)]



Chromatogram (Zoom)



Spectrum

Line#:1 R.Time:0.150(Scan#:1)
MassPeaks:430
RawMode:Single 0.150(1) BasePeak:32.05(685)
BG Mode:None Group 1 - Event 1

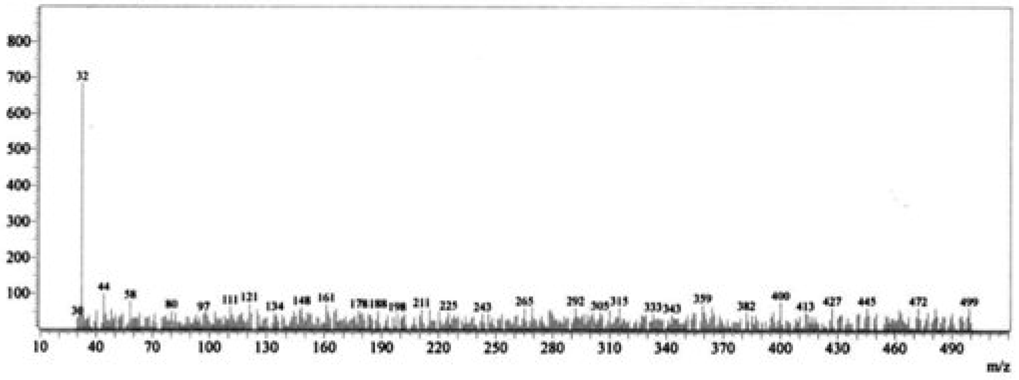
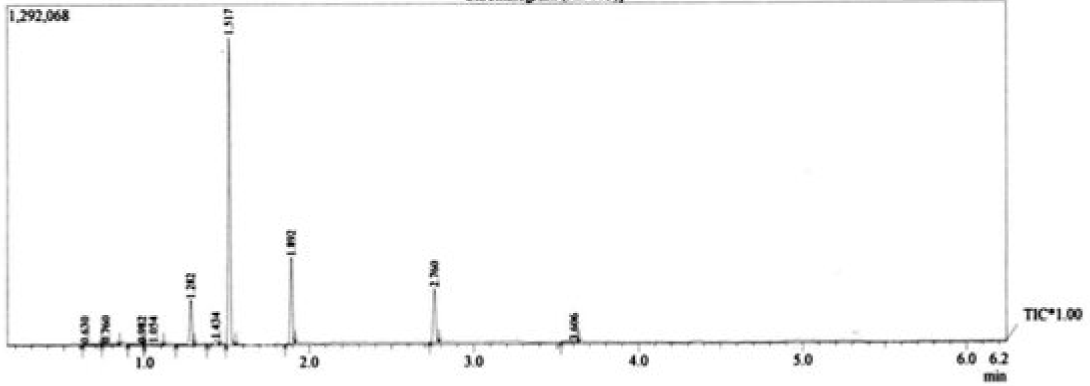
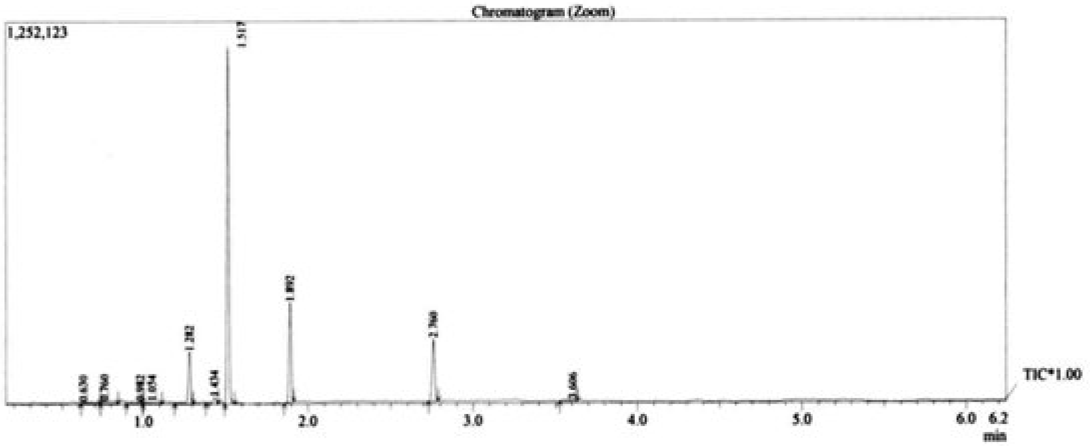


Figure: 5.20

Chromatogram (All TIC)]

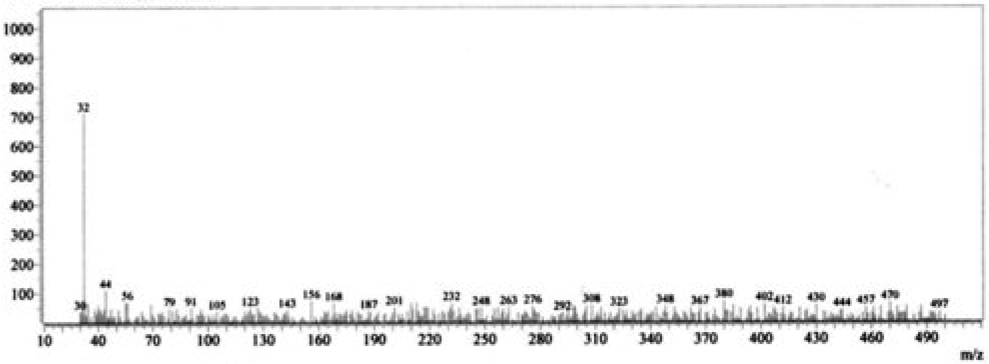


Chromatogram (Zoom)



Spectrum

Line#:1 R.Time:0.150(Scan#:1)
MassPeaks:418
RawMode:Single 0.150(1) BasePeak:32.05(712)
BG Mode:None Group 1 - Event 1



Chapter 6: Conclusions with Future Prospects

6. Entire thesis will be concluded here giving important points along with future prospects.

6.1. Conclusions

- CuO, Fe_2O_3 and Al_2O_3 nano catalysts were synthesized and categorized using various characterization techniques (SEM, XRD and PSA).

- Catalysts were used in bulk and in nano form for comparative study.

- More quality and quantity of cracked product and gases were observed when nano catalysts were used.

- A prominent cracking of Naphtha into "Butane, Methyl Hexane, Cyclopentane, Methyl Pentane and Methyl Cyclohexane" was observed while cracking under sunlight.

6.2. Future Plans

Petroleum field is very demanding so any minute improvement in its refining will be of much greater help to the industry and will help to withstand the speedy depletion of crude resources.

6.2.1. **Plant Design**

For ultimate success and ultimate quality product, designing a proper plant which caters for the temperature control and safety of catalyst and product is of utmost importance. Successful plant designing will encourage for further research in this very project (relating to petroleum) which has very tough competition and demand ahead. As catalysts used here are of nano size which require a precise design of plant as to prevent any waste of nano catalysts. Moreover, increase in demand of crude resources and speedy depletion of natural reservoirs demands a detailed designing and thought full research on the petroleum field to comply with increasing petroleum demands.

6.2.2. **Catalyst's Regeneration**

In order to get the maximum output from the least input in regard of both quality and quantity catalyst plays an important role. Petroleum refining started using catalysts in the bulk form which is now on its verge to shift to nano regime keeping its obvious results in view. However, nano catalyst being very fine in its geometry and precious due to its difficult preparation and cost are required to be regenerated after use and prevented from any unwanted wastage.

Bibliography

1. GUPTA, O.P., *Elements of fuels, furnaces and refracatories*. Fourth ed. Vol. I. 2000, 2-B, Nath Market, Nai Sarak, Delhi-110006: Romesh Chandaer Khanna for Khana Publishers. 955.
2. Antos, G.J. and A.M. Aitani, *Catalytic naphtha reforming*. Vol. 100. 2004: CRC Press.
3. Konno, H., et al., *Effectiveness of Nano-scale ZSM-5 Zeolite and its Deactivation Mechanism on Catalytic Cracking of Representative Hydrocarbons of Naphtha.* Microporous and Mesoporous Materials, 2013.
4. Konno, H., et al., *Effectiveness of nano-scale ZSM-5 zeolite and its deactivation mechanism on catalytic cracking of representative hydrocarbons of naphtha.* Microporous and Mesoporous Materials, 2013. 175: p. 25-33.
5. Keyvanloo, K., A. Mohamadalizadeh, and J. Towfighi, *A novel CeO2 supported on carbon nanotubes coated with SiO2 catalyst for catalytic cracking of naphtha.* Applied Catalysis A: General, 2012. 417–418(0): p. 53-58.
6. Fathi, M.M. and P. Pereira-Almao, *Kinetic Modeling of Arab Light Vacuum Residue Upgrading by Aquaprocessing at High Space Velocities.* Industrial & Engineering Chemistry Research, 2013. 52(2): p. 612-623.
7. Mendoza de la Cruz, J.L., et al., *Measurements and correlation of Mexican heavy dead crude oil viscosities.* Journal of Petroleum Science and Engineering, 2013. 110(0): p. 184-192.
8. Speight, J.G., *Chapter 7 - Heavy Feedstock Refining—The Future*, in *Heavy and Extra-heavy Oil Upgrading Technologies*, J.G. Speight, Editor. 2013, Gulf Professional Publishing: Boston. p. 149-162.
9. Li, D., *Crucial technologies supporting future development of petroleum refining industry.* Chinese Journal of Catalysis, 2013. 34(1): p. 48-60.
10. Sedighi, M., K. Keyvanloo, and J. Towfighi, *Kinetic study of steam catalytic cracking of naphtha on a Fe/ZSM-5 catalyst.* Fuel, 2013. 109(0): p. 432-438.
11. Corma, A., et al., *Different process schemes for converting light straight run and fluid catalytic cracking naphthas in a FCC unit for maximum propylene production.* Applied Catalysis a-General, 2004. 265(2): p. 195-206.

12. Pan, M., X. Li, and Y. Qian, *New approach for scheduling crude oil operations.* Chemical Engineering Science, 2009. 64(5): p. 965-983.

13. Chuachuensuk, A., et al., *A systematic model-based analysis of a downer regenerator in fluid catalytic cracking processes.* Computers & Chemical Engineering, 2013. 49(0): p. 136-145.

14. Pinheiro, M., et al., *Characterization and comparison of pore landscapes in crystalline porous materials.* Journal of Molecular Graphics and Modelling, 2013. 44(0): p. 208-219.

15. Ozalp, N., K. Ibrik, and M. Al-Meer, *Kinetics and heat transfer analysis of carbon catalyzed solar cracking process.* Energy, 2013. 55(0): p. 74-81.

16. Ozalp, N., A. Kogan, and M. Epstein, *Solar decomposition of fossil fuels as an option for sustainability.* International Journal of Hydrogen Energy, 2009. 34(2): p. 710-720.

17. Chin, C.S., A. Babu, and W. McBride, *Design, modeling and testing of a standalone single axis active solar tracker using MATLAB/Simulink.* Renewable Energy, 2011. 36(11): p. 3075-3090.

18. Singh, M.K., S. Mahapatra, and S.K. Atreya, *Solar passive features in vernacular architecture of North-East India.* Solar Energy, 2011. 85(9): p. 2011-2022.

19. Alyani, M., et al., *Thermal catalytic cracking of naphtha over multi wall carbon nanotube catalysts.* Journal of Analytical and Applied Pyrolysis, 2012. 98: p. 7-14.

20. Sedighi, M., K. Keyvanloo, and J. Towfighi, *Kinetic study of steam catalytic cracking of naphtha on a Fe/ZSM-5 catalyst.* Fuel, 2013. 109: p. 432-438.

21. Simacek, P., et al., *Fischer-Tropsch product as a co-feed for refinery hydrocracking unit.* Fuel, 2013. 105: p. 432-439.

22. Seifzadeh Haghighi, S., et al., *Investigation of ethylene production in naphtha thermal cracking plant in presence of steam and carbon dioxide.* Chemical Engineering Journal, 2013.

23. Neises, M., et al., *Solar-heated rotary kiln for thermochemical energy storage.* Solar Energy, 2012. 86(10): p. 3040-3048.

24. Kodama, T., *High-temperature solar chemistry for converting solar heat to chemical fuels.* Progress in Energy and Combustion Science, 2003. 29(6): p. 567-597.

25. Abanades, S. and G. Flamant, *Experimental study and modeling of a high-temperature solar chemical reactor for hydrogen production from methane cracking.* International Journal of Hydrogen Energy, 2007. 32(10–11): p. 1508-1515.