Production of Ethylene through Dehydration of Ethanol

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By

Muhammad Rizwan

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Supervisor: Dr. M. Ashraf Tahir

Co-Supervisor: Dr. Arshad Hussain

School of Chemical & Materials Engineering (SCME)

National University of Sciences & Technology (NUST)

Islamabad Pakistan

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Dedication

I dedicate this humble effort and studies to my beloved parents, respected teachers and sincere friends.

Abstract

Ethylene (ethene), C_2H_4, is the largest volume building block for many petrochemicals. This olefin is used to produce many end products such as plastics, resins, fibers, etc. It is mainly derived from thermal cracking of petroleum or natural gas feedstock. The cracking process requires high temperature. In recent years, with the shortage of natural resource and energy, moreover, also with the soaring prices of crude oil, the way of ethanol dehydration into ethylene over a catalyst has drawn attention compared to the traditional route because of some advantages, such as the reduction of CO_2, low production cost, and energy consumption. Plenty of molasses (a by-product of sugar industry) based ethanol is available because alcohol does not have market as a drink in country like Pakistan. In this work, a techno-economic analysis of production of ethylene from molasses based ethanol and thermal cracking of naphtha is performed and dehydration of ethanol is selected to produce ethylene. Furthermore, a laboratory experimental rig is designed and operated to carry out dehydration of ethanol in a fixed bed reactor. The dehydration reaction occurs at 315-425 ^{o}C (599-797 ^{o}F) in presence of aluminium oxide as a catalyst. A conventional purification scheme may be used to remove any trace by-product. The reaction product is collected and analyzed by specific confirmatory tests.

Acknowledgement

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Chapter 1

Introduction

1.1   Introduction

Ethylene (IUPAC name: ethene), $H_2C=CH_2$, is the largest-volume petrochemical produced worldwide. Ethylene, however, has no direct end uses, being used almost exclusively as a chemical building block. It has been recovered from coke-oven gas and other sources in Europe since 1930. Ethylene emerged as a large volume intermediate in the 1940s when U.S. oil and chemical companies began separating it from refinery waste gas and producing it from ethane obtained from refinery byproduct streams and from natural gas. Since then, ethylene has almost completely replaced acetylene for many synthesis. Ethylene is produced mainly by thermal cracking of hydrocarbons in the presence of steam, and by recovery from refinery cracked gas [1].

Ethylene is a gaseous organic compound containing a carbon-carbon double bond. Ethylene is classified as an unsaturated hydrocarbon and is widely used in industry, also as a plant harmone. Ethylene is the most produced organic compound in the world. To meet the ever increasing demand for ethylene, sharp increases in production facilities are added globally, particularly in the Persian Gulf countries and in China [2].

1.2   Structure and Bonding

This hydrocarbon has four hydrogen atoms bound to a pair of carbon atoms that are connected by a double bond. All six atoms that comprise ethylene are coplanar. The H-C-H angle is 119°, close to the 120° for ideal sp² hybridized carbon. The molecule is also relatively rigid: rotation about the C-C bond is a high energy process that requires breaking the π-bond [3].
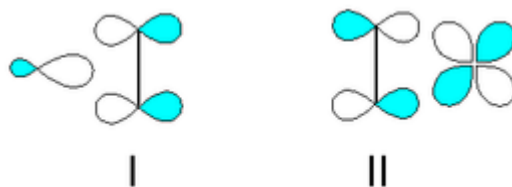
Figure 1.1: Orbital description of bonding between ethylene and a transition metal.

The π-bond in the ethylene molecule is responsible for its useful reactivity. The double bond is a region of high electron density, thus it is susceptible to attack by electrophiles [3].

1.3 Reactivity

Ethylene is a very reactive intermediate, and hence is involved in many chemical reactions. The ethylene double bond reacts readily to form saturated hydrocarbons, their derivatives, or polymers. Electrons in the π-bond are less tightly held and more easily polarized than electrons in a sigma bond. The carbon-carbon double-bond energy is 611 kJ/mol (146 kcal/mol), which is less than twice the C–C bond dissociation energy of 368 kJ/mol (88 kcal/mol) found in ethane. The C–H bond dissociation energy is 452 kJ/mol (108 kcal/mol), and approximate acidity as measured by K_a, acidity constant, is 10^{-45}. Therefore, ethylene reacts with electrophilic reagents like strong acids (H^+), halogens, and oxidizing agents, but not with nucleophilic reagents such as Grignard reagents and bases. Some of the reactions have commercial significance and others have only academic interest [3].

The principal reactions with commercial significance include polymerization, oxidation, and addition including halogenation, alkylation, oligomerization, hydration, and hydroformylation [3].

1.4 Physical Properties of Ethylene

Ethylene is a colorless, non-corrosive, flammable gas with a faint, sweet odor at ambient temperature and pressure. Data pertaining to physical properties of ethylene is presented in Table 1.1 [1].

Property	Value
Physical State	Gas, liquid under pressure
Color	Colorless gas
Odor	Faint, sweet
Molecular Formula	C_2H_4
Molecular Weight	28.05 g/mol

Normal Boiling Point (at 1 atm)	-103.71°C
Melting Point	-169.15 °C
Flash Point	-136 °C
Autoignition Temperature	542.8 °C
Critical Temperature	9.90 °C
Critical Pressure	5.117 MPa
Critical Density	0.21 g/cm^3
Critical Compressibility Factor	0.2812
Density at Boiling Point	0.57 g/cm^3
Density at 0 °C	0.34 g/cm^3
Density at STP	1.2603 g/L
Density relative to Air	0.9686
Molar Volume at STP	22.258 L
Surface Tension at Boiling Point	16.5 mN/m
Surface Tension at 0 °C	1.1 mN/m
Heat of Fusion	119.5 KJ/Kg
Heat of Combustion	47.183 MJ/Kg
Heat of Vaporization at Boiling Point	488 KJ/Kg
Heat of Vaporization at 0 °C	191 KJ/Kg
Specific Heat of Liquid at Boiling Point	2.63 KJ/Kg.K
Specific Heat of Gas at T_C	1.55 KJ/Kg.K
Enthalpy of Formation	52.32 KJ/mol
Entropy	0220 KJ/mol.K
Thermal Conductivity at 0 °C	177 x 10^{-4} W/m.K
Thermal Conductivity at 100 °C	294 x 10^{-4} W/m.K
Thermal Conductivity at 400 °C	805 x 10^{-4} W/m.K
Viscosity of Liquid at Melting Point	0.73 mPa.s
Viscosity of Liquid at Boiling Point	0.17 mPa.s
Viscosity of Liquid at 0 °C	0.07 mPa.s

Viscosity of Gas at Melting Point	36×10^{-4} mPa.s
Viscosity of Gas at 0 ^{o}C	93×10^{-4} mPa.s
Viscosity of Gas at 150 ^{o}C	143×10^{-4} mPa.s
Vapor Pressure at -150 ^{o}C	0.002 MPa
Vapor Pressure at Boiling Point	0.102 MPa
Vapor Pressure at -50 ^{o}C	1.10 MPa
Vapor Pressure at 0 ^{o}C	4.27 MPa
Explosive Limit in Air at 0.1 MPa and 20 ^{o}C	
Lower	2.75 %
Upper	28.6 %

Table 1.1: Physical Properties of Ethylene.

1.5 Uses of Ethylene

Ethylene is the raw material used in the manufacture of polymers such as polyethylene (PE), polyethylene terephthalate (PET), polyvinyl chloride (PVC) and polystyrene (PS) as well as fibers and other organic chemicals. These products are used in a wide variety of industrial and consumer markets such as the packaging, transportation, electrical/electronic, textile and construction industries as well as consumer chemicals, coatings and adhesives.

The largest outlet, accounting for 60% of ethylene demand globally, is polyethylene. Low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) mainly go into film applications such as food and non-food packaging, shrink and stretch film, and non-packaging uses. High density polyethylene (HDPE) is used primarily in blow moulding and injection moulding applications such as containers, drums, household goods, caps and pellets. HDPE can also be extruded into pipes for water, gas and irrigation, and film for refuse sacks, carrier bags and industrial lining.

The next largest consumer of ethylene is ethylene oxide (EO) which is primarily used to make ethylene glycol. Most monoethylene glycol (MEG) is used to make polyester fibers for textile applications, PET resins for bottles and polyester film. MEG is also used in antifreeze

applications. Other EO derivatives include ethyoxylates (for use in shampoo, kitchen cleaners, etc), glycol ethers (solvents, fuels, etc) and ethanolamines (surfactants, personal care products, etc).

Ethylene dichloride (EDC) is made by the chlorination of ethylene and can then be cracked to make vinyl chloride monomer (VCM). Nearly all VCM is used to make polyvinyl chloride which has its main applications in the construction industry.

Ethylene can be reacted with benzene to make ethylbenzene which is further processed into styrene. The main outlets for styrene are polymers and synthetic rubbers such as polystyrene, acrylonitrile-butadiene-styrene (ABS) and styrene butadiene rubber (SBR).

Other ethylene derivatives include alpha olefins which are used in LLDPE production, detergent alcohols and plasticizer alcohols; vinyl acetate monomer (VAM) which is used in adhesives, paints, paper coatings and barrier resins; and industrial ethanol which is used as a solvent or in the manufacture of chemical intermediates such as ethyl acetate and ethyl acrylate.

Ethylene is one of the largest-volume petrochemicals. With a diverse range of end-uses, demand is sensitive to both economic and energy cycles. It is often seen as a barometer to the performance of the petrochemical industry as whole.

According to US-based SRI Consulting, global production and consumption of ethylene in 2009 were both approximately 112 million tonnes. Global capacity utilization was 85.3% in 2009, down from 87% in 2008. Ethylene consumption is estimated to have increased by 1.3% in 2009; it is forecast to grow an average 4.1%/year up to 2014, slowing to 3.4%/year from 2014 to 2019 [4].

Middle East, China and the US

According to ICB, between 2010 and 2016, the Middle East and China will account for 24.9 million tonnes/year of new ethylene capacity out of a total 30.5 million tonnes/year. As a result, over 80% of the new ethylene production start ups will be in the Middle East and China.

In China, examples of projects include Fushun Petrochemical's 800,000 ton/year ethylene plant for start-up in 2012, and Kuwait Petroleum/Sinopec's 1 million ton/year ethylene plant expected to start up in 2015.

Saudi Arabia has three cracker projects in the pipeline – Saudi Polymers' 1.2 million tonnes/year ethylene project with startup due in 2011, a 30% expansion by PetroRabigh and the delayed Dow Chemical and Saudi Aramco 1.2 million tonnes/year ethylene project, which originally had a startup date of 2015. With supplies of ethane for new crackers expected to be limited, new projects such as the Dow/Saudi Aramco cracker are likely to be based on other feedstocks such as naphtha.

In Abu Dhabi, the Borouge III ethane cracker which will produce 1.5 million tonnes/year of ethylene is expected to start up 2014.

Other ethylene projects in the pipeline include Braskem and Grupo Idesa's $2.5bn 1 million ton/year ethylene XXI project in Mexico, which is expected to start up in 2015 [4].

Ethylene as a Ripening agent for Fruits and Vegetables

It affects the growth, development, ripening, and senescence (aging) of all plants. It is normally produced in small quantities by most fruits and vegetables. Many fruits produce larger quantities of ethylene and respond with uniform ripening when exposed to an external source of ethylene.

Ethylene gas is used commercially to ripen tomatoes, bananas, pears, and a few other fruits postharvest. Ethylene can be explosive if it reaches high concentrations, so it has to be used cautiously [4].

1.6   Storage, Handling and Shipment of Ethylene

Storage

There are two basic types of vessels used to store ethylene: pressurized or cylindrical (bullet tanks) and flat bottom storage tanks. The most common way to store liquid ethylene is in flat bottom insulated tanks at atmospheric pressure (temperature is -150°F). For smaller capacities,

liquid ethylene can be stored in pressurized vessels (cylinders or spheres). They are generally constructed to (ASME) Boiler & Pressure Vessel Code.

Ethylene is also stored as a supercritical fluid (ambient temperature, pressure in excess of 1000 psig) below ground in caverns created within dense salt dome formations. A cavern is formed by drilling into the salt formation and then washing the cavern with fresh water.

Care must be exercised to select the proper material of construction for the storage tank. Carbon steel is typically used for pressurized spheres when subjected to the proper tests for impact and ductility. There exists a wide variety in grades of steel; generally, carbon steel will be suitable for temperatures down to -50° F. Older installations may be suitable only for temperatures down to -25° F. Stainless steel or other low temperature alloys must be used for storage at lower temperatures [5].

Handling

Ethylene presents a significant fire and explosion hazard based on its physical properties, including flashpoint, vapor pressure, and boiling point. It can quite readily form explosive mixtures in air as a result of its high vapor pressure. Therefore, preventive measures must be taken to minimize the potential for a fire or explosion.

Ethylene is extremely flammable and is classified as a flammable gas. Ethylene concentrations in air of between 2.3% and 32.3% can form explosive mixtures. If an ignition source is present, a fire and/or explosion can result. At temperatures of approximately 842 ^{o}F or above, this material can autoignite. In other words, it can spontaneously ignite without the application of flame or spark if it is heated above this temperature.

Vapors of ethylene are slightly lighter than air (0.975 w/air =1). A vapor with a vapor density less than 1 is lighter than air and would tend to rise in air. An ethylene gas release may produce a visible fog when it is escaping in a non-fire emergency situation such as a spill or leak. In a fire situation, conditions can develop which could lead to explosions and further fire propagation.

The build-up of pressure in closed containers of ethylene caused by elevated temperatures can result in container failure. Ethylene will polymerize but only at elevated temperature and pressure in the presence of a catalyst.

A particular concern for ethylene pipeline maintenance is the possible overheating and consequent initiation of a decomposition reaction in the pipeline. After offline maintenance is conducted on the pipeline, it normally is purged with nitrogen prior to refilling with ethylene. Care must be taken when refilling the pipeline to avoid rapid compression of the ethylene vapor as the pipeline is filled up to the vapor pressure of approximately 750 psig. Repressuring gradually allows heat dissipation and prevents the ethylene from reaching autodecomposition temperature. The decomposition reaction, if started, will almost certainly result in a pipeline failure.

So Care must be taken in the handling and disposal of laboratory-sized and larger samples of ethylene. Laboratory and sample storage facilities should be appropriate for the associated risks. Test and handling procedures should be clear and the laboratory and operating personnel well trained [5].

Shipment

Most ethylene is transported by pipelines to and from various production sites but in certain cases it is transported by cargo tank or rail tank cars to reach its destination [5].

1.7   Specification and Analysis

Polyethylene is the predominant derivative of ethylene requiring very high purity (99.9% plus). A typical polymer-grade specification is given in Table 1.2. Almost all ethylene plants use gas chromatography or gas chromatography combined with mass spectrometry for analysis. For specific impurities like sulfur, water, and other hydrocarbons and elements, ASTM standard tests are recommended (D2504-67, D2505-67, 2785-70, E203-75) [3].

Component	Value
ethylene, mol%, min	99.95
methane + ethane	balance
other impurities, mol ppm, max	
hydrogen	5.0
acetylene	1.0
Oxygen	1.0
carbon monoxide	1.0
carbon dioxide	1.0
Propylene	10.0
C_4+	10.0
Water	2.0
total sulfur	2.0
Methanol	5.0
total chlorine	2.0
DMF	1.0
other compounds	5.0

Table 1.2: Specification for Polymer Grade Ethylene.

1.8   Emergency Response and Planning

During transport, and also during normal plant operations, a release may occur from an incident that damages the container and results in an ethylene leak. Gases or liquefied gases of this type are normally processed in equipment and stored in tanks equipped with pressure relief devices. These devices are designed to release a small amount of the material if the pressure in the tank

goes above a preset limit. Use of pressure relief devices greatly reduces the risk of a tank or vessel rupture in the event of pressure building inside the tank. Use of flares or other control devices to which the relief devices can discharge can reduce the risk of releases to the atmosphere. When released from a tank to the atmosphere, liquid ethylene will become a gas. Due to the storage pressure and low temperature of the material, it can appear like steam. Because it is lighter than air, it will rise and then mix with the air and seem to disappear. When these releases occur, emergency response measures need to be set in motion as appropriate for the size of the release.

A thorough emergency response plan will address all aspects of an ethylene emergency, including problems that may be specific to a particular site. Effective emergency response plans are generally tested through periodic drills that involve emergency response personnel both on-site and in the local community. Appropriate response procedures for responding to spills may include the following measures [5]:

- Remove or shut off all sources of ignition.
- Prevent spill from entering sewers and waterways.
- Wear goggles, respirators, rubber overclothing, and gloves.
- Evacuate area in case of large discharge.
- Stay upwind and use water spray to disperse vapors.
- Notify fire department and local health and pollution control agencies.

1.9   Methods of Ethylene Production

The following methods are used to produce ethylene gas [1].

1.9.1 Cracking of Hydrocarbons

Thermal cracking of hydrocarbons is the principal route for the industrial production of ethylene. In thermal cracking, valuable by-products including propylene, butadiene, and benzene are also produced. Commercially less valuable methane and fuel oil are also produced in significant

proportions. An important parameter in the design of commercial thermal cracking furnaces is the selectivity to produce the desired products.

From Ethane

Ethane is obtained from wet natural gases and refinery waste gases. This ethane is cracked with steam as s diluents in furnace. The furnace effluent is quenched in a heat exchanger and further cooled by direct contact in a water quench tower where the diluents steam is condensed. The cracked gas is compressed, acid constituents are removed and the purified gas dried. Methane and hydrogen are removed from the pyrolysis products in the demathanizer. The product stream is hydrogenated to remove acetylene. Ethylene is separated in the ethylene tower from the un-reacted ethane and higher boiling products.

In the manufacture of ethylene from ethane, the energy requirement for utilities is higher. This process can give 85- 90% yield of ethylene but cracking of ethane is comparatively difficult.

From Propane

The supply of ethane can be increased by deeper ethane extraction from natural gas but the supply of propane to be used for olefin production is not encouraging. The maximum propane extraction from natural gas is essentially quantitative and utilization of this propane is primarily as a fuel.

Propane can be cracked at low operating conditions and give almost same yield as that from ethane. So cracking of propane is easier than ethane but the separation of by-products is more extensive.

From Ethane-Propane Mixture

Ethylene can also be produced by the cracking of mixtures of ethane and propane. The rate of cracking of ethane is found to be decreased by the addition of propane, while the rate of propane cracking is slightly increased by the presence of ethane.

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From N-Butane

N-butane is a minor source of ethylene production. Large by-products are formed which make recovery of ethylene more expensive and difficult.

From Liquefied Petroleum Gas (LPG)

Ethylene can be produced from LPG in the areas where liquefied petroleum gas is produced in excess.

From Gas Oil and Crude Oil

The cracking of gas oil to produce olefins is an old art. Gas oils, in general, are not as desirable as naphtha for the production of ethylene. They have a higher density than naphtha, lower hydrogen content, higher sulfur content and a higher concentration of aromatic compounds. Cracking of gas oil and crude oil give low yield and large amount of by-product.

1.9.2 From Naphtha

Ethylene can be produced from naphtha by thermal cracking i.e. so-called steam cracking. To cope with the requirements of high temperature and reduced residence time, the steam cracking process has been modified in various ways to improve energy efficiency, e.g., the cracking furnace (radiant tubes and coils) and heat recovery systems. The current steam cracking process uses as much as 40% of the energy consumed by the entire petrochemical industry.

One of the disadvantages of naphtha over gas feed stock is the wider spectrum of by-products so it gives low yield of ethylene.

1.9.3 From Dehydration of Ethanol

Alcohols when dehydrated in the presence of a catalyst give alkenes. The best procedure is that the vapors of ethanol are passed over heated catalyst usually alumina

In this work, a techno-economic analysis of ethylene production by dehydration of ethanol and thermal cracking of naphtha is reported. Based on this analysis, dehydration of ethanol is selected to produce ethylene and a laboratory experimental rig is designed to carry out dehydration of ethanol.

Chapter 2

Techno-Economic Analysis of Production of Ethylene from Thermal Cracking of Naphtha and from Dehydration of Ethanol

2.1 Production of Ethylene through Cracking of Naphtha

Light olefins, ethylene and propylene, are produced commercially via steam cracking of various hydrocarbons, such as ethane, naphtha, and gas oil. These low molecular weight olefins are among the most important base chemicals for the petrochemical industry. Modern steam cracking plants today typically are the center of petrochemical complexes producing 500 000 – 1 000 000 tons per year of ethylene, the main petrochemical building block. Ethylene yield on a weight basis is typically 30% with naphtha feedstock and goes down to 25% for gas oil feedstock [6].

2.1.1 Process Description of Naphtha Cracking

Steam cracking typically refers to all processes inside the battery limits of a steam cracker. Steam cracker is comprised of the following three sections as shown in Figure 2.2 [7].

- Pyrolysis
- Primary fractionation/compression
- Product recovery/separation

2.1.1.1 Pyrolysis Section

This is the heart of a steam cracker. Naphtha first enters the convection section of a pyrolysis furnace, where a series of heat exchangers are located and it is preheated to 650 ^{o}C. Then, naphtha is vaporized with superheated steam and is passed into long (12–25 m), narrow (25– 125 mm) tubes, which are made of chromium nickel alloys. Pyrolysis takes place mainly in the radiant section of the furnace, where tubes are externally heated to 750–900 ^{o}C (up to 1100 ^{o}C) by fuel oil or gas fired burners. Depending on the severity, naphtha is cracked into smaller molecules via a free-radical mechanism in the absence of catalysts. The free radicals lead to the formation of light olefins in the gaseous state. After leaving the furnace, the hot gas mixture is subsequently quenched in the transfer line exchangers (TLE) to 550–650 ^{o}C, or sometimes lowers to 400 ^{o}C. TLE will then be followed by a series of heat exchangers and temperatures can drop down to 300 ^{o}C. These heat transfer activities avoid degradation by secondary reactions and
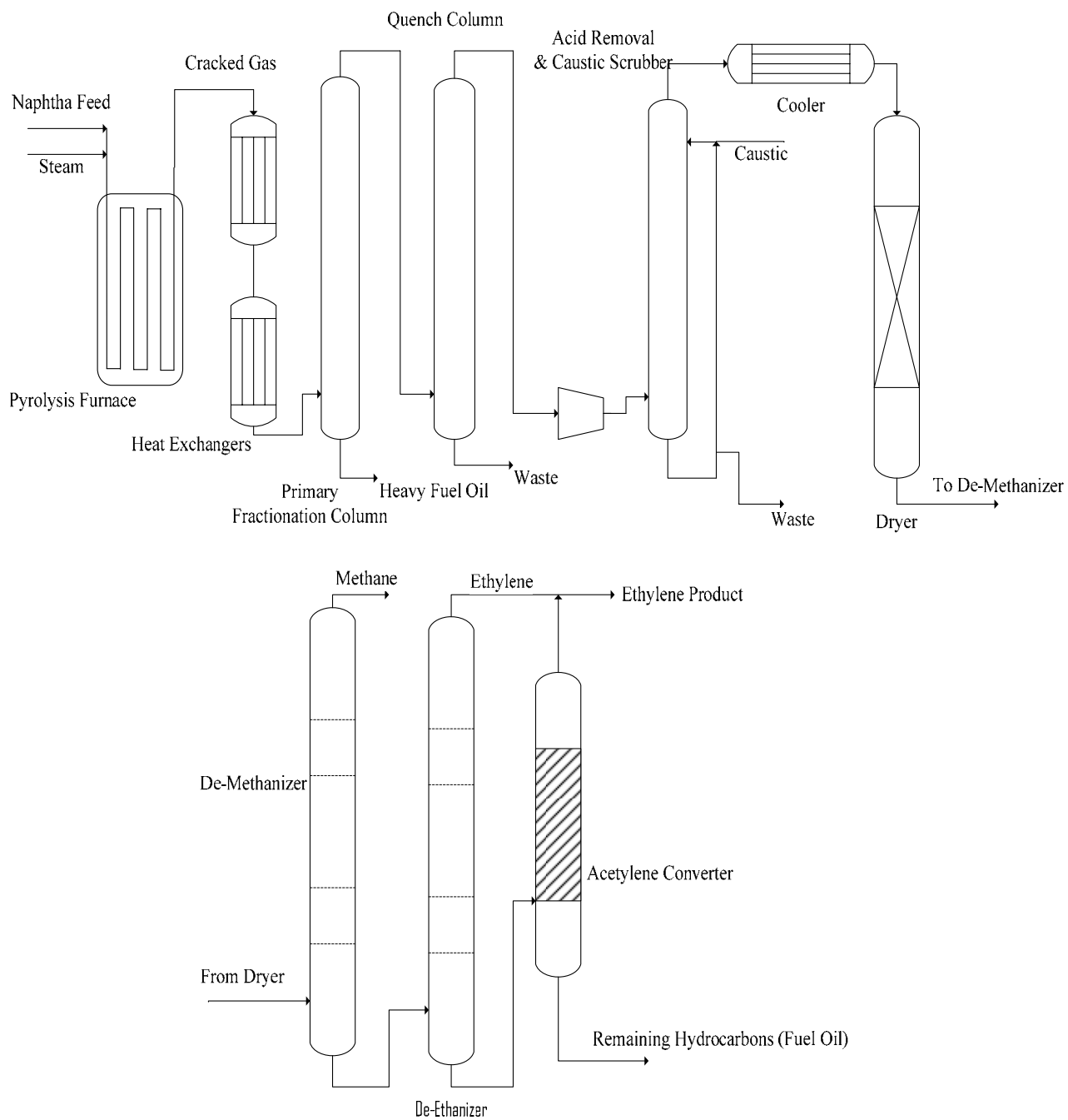
Figure 2.2: Process Flow Diagram of Naphtha based Ethylene Production.

at the same time generate high pressure steam for driving compressors, etc. However, heat exchangers are prone to fouling and therefore need both scheduled and unscheduled shutdowns.

Chemical Reactions in Pyrolysis Section

A number of reactions take place in the pyrolysis section of naphtha cracker. The reaction mechanism of thermal cracking of hydrocarbons is generally accepted as free radical chain reactions. Typical reactions occurring during thermal cracking of naphtha are [8],

Radical Reactions

1) Initiation reactions

Unimolecular: $CH_3-CH_2-CH_2-CH_2-CH_3 \longrightarrow C_3H_7\cdot + C_2H_5\cdot$

Bimolecular: $CH_3-CH_3 + CH_2 = CH_2 \longrightarrow C_2H_5\cdot + C_2H_5\cdot$
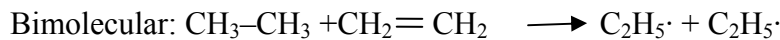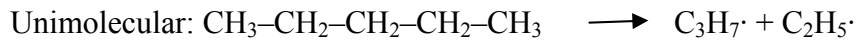
2) Propagation reactions

Radical decomposition: $CH_2\cdot-CH_2-CH_3 \longrightarrow C_2H_4 + CH_3\cdot$

Radical isomerization: $CH_2\cdot -CH_2-CH_2-CH_2-CH_3 \longrightarrow CH_3-CH_2-CH_2-CH\cdot - CH_3$

H-abstraction on molecules: $CH_3\cdot + CH_3-CH_3 \longrightarrow CH_4 + C_2H_5\cdot$

Addition of radicals on unsaturated molecules: $CH_3\cdot + CH_2 = CH_2 \longrightarrow CH_3-CH_2- CH_2\cdot$
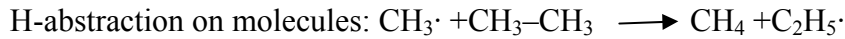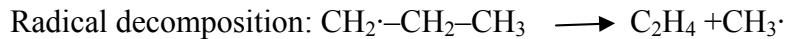
3) Termination reactions: Recombination of radicals to form a molecule.

$CH_3\cdot + CH_3\cdot \longrightarrow CH_3-CH_3 C_2H_5\cdot + C_2H_5\cdot \longrightarrow CH_3-CH_3 + CH_2 = CH_2$

Molecular Reactions

Olefin isomerization: $CH_3-CH = CH-CH_3 \longrightarrow CH_2 = CH-CH_2-CH_3$

Olefin dehydrogenation: $CH_2 = CH-CH_2-CH_3 \longrightarrow CH_2 = CH-CH = CH_2 + H_2$

Olefin decomposition: $CH_2 = CH-CH_2-CH_2-CH_3 \longrightarrow CH_2 = CH-CH_3 + CH_2 = CH_2$

Diels-Alder reaction: $CH_2 = CH-CH = CH_2 + CH_2 = CH_2 \longrightarrow$ Cyclo C_6H_{10}
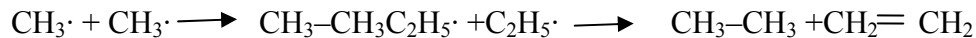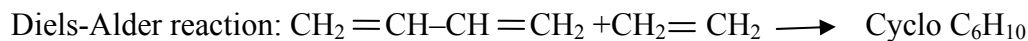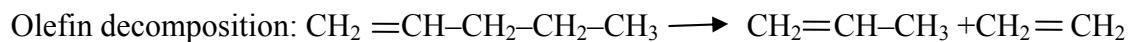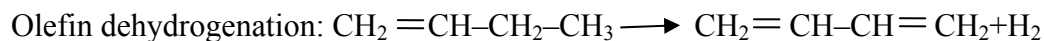
2.1.1.2   Primary Fractionation/Compression

Primary fractionation applies to naphtha and gas oil feed only. In the primary fractionation section, gasoline and fuel oil streams (rich in aromatics) are condensed and fractionated. While this liquid fraction is extracted, the gaseous fraction is de-superheated in the quench tower by a circulating oil or water stream. The gaseous fraction is then passed through four or five stages of gas compression with temperatures at approximately 15–100 ^oC, then cooling and finally cleanup to remove acid gases, carbon dioxide and water. Most of the dilution steam is condensed, recovered and recycled. Products of this section are fuel oil and BTX, or aromatic gasoline which contains benzene, toluene and xylene. A common problem with compression is fouling in the cracked gas compressors and after-coolers. The build-up of polymers on the rotor and other internals results in energy losses as well as mechanical problems. Wash oil and water are used to reduce fouling.

2.1.1.3   Product Recovery/Separation

This is essentially a separation process through distillation, refrigeration and extraction. Equipment includes chilling trains and fractionation towers, which include refrigeration, de-methanizer, de-ethanizer. De-methanization requires very low temperatures, e.g. -114 ^oC. C_2 compounds, or ethylene and ethane, separation often requires large distillation columns with 120 – 180 trays and high reflux ratios. Undesired acetylene is removed through catalytic hydrogenation or extractive distillation. Similarly, C_3 compounds, or propane and propylene, are re-boiled with quench water at approximately 80 ^oC and separated in the C_3 splitter. Ethylene and propylene refrigeration systems can be operated at low temperatures within -10 and -150 ^oC for cooling and high pressure with 15–30 bar for compression. Ethane and propane are recycled as feedstock. Methane and hydrogen are separated at cryogenic temperatures. As fuel grade by-products, they are often used as fuel gas in the pyrolysis process, but they can also be exported. Butadiene, other C_4 compounds and aromatic gasoline are separated in the end. The total product yields from naphtha cracking differ depending on the paraffin and aromatic content of the naphtha and on the severities. Generally, steam cracking of ethane and other feedstocks also requires three sections that are similar to those in the case of naphtha cracking process. However, the processes differ depending on feedstock properties and design arrangement, which often

influence fractionation and separation sections. For instance, ethane cracking requires slightly higher temperature in the furnace, a higher capacity of the C_2 splitter but less infrastructure facilities. Storage tanks or recovery equipment for propylene, butadiene and BTX aromatics are not needed, but an ethane vaporizer and super-heater are required.

An additional issue is coking. Regular decoking is required in various parts of the pyrolysis section. Before decoking, the furnace has to be shut down. Then, high pressure steam and air are fed to the furnace while it is heated up to 880–900 $^{\circ}$C, or even up to 1100 $^{\circ}$C. Coke on the inner surfaces of the wall and tubes is either burned off, washed away with high pressure water or removed mechanically. Decoking process can take 20–40 h for a naphtha steam cracker. Depending on the feedstocks, coil configuration and severity, decoking for steam cracking furnaces is required every 14–100 days on an average. Typically, a naphtha pyrolysis furnace is decoked every 15–40 days. Maximum cycle time is around 60–100 days. Decoking is also required for quench towers, TLEs and other sections.

2.1.1.4   Energy Consumption

Basic chemicals such as ethylene, propylene, and other light olefins are currently manufactured mainly from naphtha by thermal cracking, i.e., so-called steam cracking. To cope with the requirements of higher-temperature and reduced residence time, the steam cracking process has been modified in various ways to improve energy efficiency, *e.g.*, the cracking furnace (radiant tube and coils) and heat recovery systems. However, marginal technological improvements cannot make further improvement in energy efficiency. The current steam cracking process uses as much as 40% of the energy consumed by the entire petrochemical industry. Therefore, global environmental issues have stimulated the development of processes that maximize energy and resource-savings and minimize CO_2 emissions. Besides, in the case of the current steam cracking process, it is difficult to control the composition of olefins formed. Hence, there is an increasing demand for processes capable of controlling the composition of olefins.

2.2   Cost Estimation of Ethylene Production through Cracking of Naphtha

Cost estimation of ethylene production through cracking of naphtha designed to produce 30 metric ton/day of ethylene as shown in Figure 2.2 has been estimated [9, 10].

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2.2.1 Purchased Cost of Equipments:

Purchased cost of major equipment items for naphtha based ethylene production plant is estimated and is given in Table 2.3.

S. No.	Equipments	Specifications	Cost in US$
1	Furnace	Heat duty = 2800 KW	50000
2	Reactor	L = 20 m, D = 0.125 m	20000
3	Heat exchanger-I	Heat transfer area = 65 m^2	8500
4	Heat exchanger-II	Heat transfer area = 96 m^2	10500
5	Fractionation column	L = 21 m, D = 2 m	20500
6	Quenching column	L = 12 m, D = 2 m	14000
7	Compressor	Multistage, reciprocating	30000
8	Scrubber	L = 21 m, D = 2 m	20500
9	Cooler	Heat transfer area = 9 m^2	2500
10	Dryer	L = 10 m, D = 2m	12500
11	De-methanizer	L = 22.86 m, D = 2 m	14000
12	Acetylene converter	L = 6.3 m, D = 1 m	11000
13	De-ethanizer	L = 18.2 m, D = 2 m	11200
Total purchased equipment cost (year 2004)			**225200 $**

Table 2.3: Purchased Cost of Naphtha Based Ethylene Production Plant.

Chemical engineering cost index in 2004   =   444.2

Chemical engineering cost index in 2009   =   575.4

Now, by using following equation,

$$\text{Puchased equipments cost in US\$} = \text{Cost in 2004} \times \frac{\text{cost index in 2009}}{\text{cost index in 2004}}$$

Purchased equipment cost ($)   =   291715.62 $

2.2.2 Direct Cost

a. Purchased equipment cost (PEC)   =   291715.62 $

b. Purchase Equipment Installation (47% of a)   =   137106.34 $

c. Instrumentation and control (36% of a)   =   105017.62 $

d. Piping Cost (68% of a)   =   198366.62 $

e. Electrical Systems (11% of a)   =   32088.71 $

f. Building (18% of a)   =   52508.81 $

g. Yard Improvement (10% of a)   =   29171.56 $

h. Service Facility (70% of a)   =   204200.93 $

A. Total direct cost (a+b+c+d+e+f+g+h)   =   1050176.24 $

2.2.3 Indirect Cost

i. Engineering and Supervision (33% of a)   =   96266.15 $

j. Construction expenses (41% of a)   =   119603.40 $

k. Legal Expenses (4% of a)   =   11668.62 $

l. Contractor's Fee (22% of a)   =   64177.43 $

m. Contigency (44% of a)   =   128354.87 $

B. Total indirect cost (i+j+k+l+m)   =   420070.49 $

2.2.4 Total Fixed Capital Investment

Total fixed capital investment is the sum of direct cost and indirect cost

C. Total fixed capital investment (A+B) = 1470246.74 $

2.2.5 Working Capital

D. Working capital (89% of a) = 259626.90 $

2.2.6 Total Capital Investment

Total capital investment is the sum of fixed capital investment and working capital

E. Total capital investment (C+D) = 1729873.64 = 1.72 million $

2.2.7 Production Cost

2.2.7.1 Variable Production Cost

n. Raw material (naphtha) = 13999705.6 $

o. Fuel oil = 1005420.8 $

p. Steam = 52000 $

q. Cooling water = 2110.4 $

r Operating labor = 490590 $

s. Operating supervision (15 % of r) = 73588.5 $

t. Maintenance and repair (7 % of C) = 102917.27 $

u. Operating supplies (15 % of t) = 15437.59 $

v. Laboratory charges (15 % of r) = 73588.5 $

F. Total variable production cost (n+o+p+q+r+s+t+u+v) = 15815358.66 $

2.2.7.2 Fixed Production Cost

w. Taxes (2 % of C) = 29404.93 $

x. Insurance (1 % of C) = 14702.46 $

y. Depreciation [(a + f)/20] = 17211.22 $

G. Total fixed production cost (w+x+y) = 61318.62 $

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| H. Plant overhead (50 % of r) | = | 245295 $ |

Total production cost = Variable production cost + fixed production cost + plant overhead

| So, Total annual production cost (F+G+H) | = | 16121972.29 $ = 1.61 million $ |

| Annual production | = | 10950 ton/year |

| Production cost per unit of ethylene ethylene | = | 1472.32 $/ton = 1.47 $/Kg of |

2.3   Production of Ethylene through Dehydration of Ethanol

Ethylene is produced by the catalytic dehydration of ethanol. In 2010 Braskem started a full-scale ethanol dehydration plant in Brazil (Braskem, 2010). The ethanol dehydration process basically consists of a reactor and several purification steps. The Braskem patent mainly focuses on the reactor, which is adiabatic. The reactor feed is diluted with steam to a large extent. The patent reveals limited information and the heat exchanger network are specified. Halcon SD developed a process in the 1960's that is used by the process plant supplier Chematur International AB (Chematur AB). Research has been performed and published on the process, i.e. some process data is available.

Figure 2.1 illustrates an overview of ethanol based ethylene production configuration investigated in the study. The process configuration is based on a literature review [11].

Ethanol is assumed to be purchased. Accordingly, for ethanol dehydration to ethylene plant, the incoming ethanol feed is in liquid phase and thus requires vaporization prior to entering the reactor. A multi-bed adiabatic reactor system consisting of four reactors in series with a SynDol catalyst bed in each reactor is assumed. The feed to each reactor is heated to 350°C - 450°C in a furnace. The reactor effluent is cooled with spraying water in the quench tower; consequently water present in the gas is condensed. It is assumed that there is access to a refrigeration medium allowing a condenser temperature of -25°C in the ethylene column. The operating pressure of the column is set to 24.5 bar. In order to achieve desired operating conditions in the ethylene column, the pressure is increased to 27 bar in a multi-stage compressor with a pressure ratio of 3 between inlet and outlet of each stage. After purifying ethylene from CO_2 (by absorption in the caustic tower with NaOH) the remaining water is removed in a dryer (i.e. a molecular sieve). The
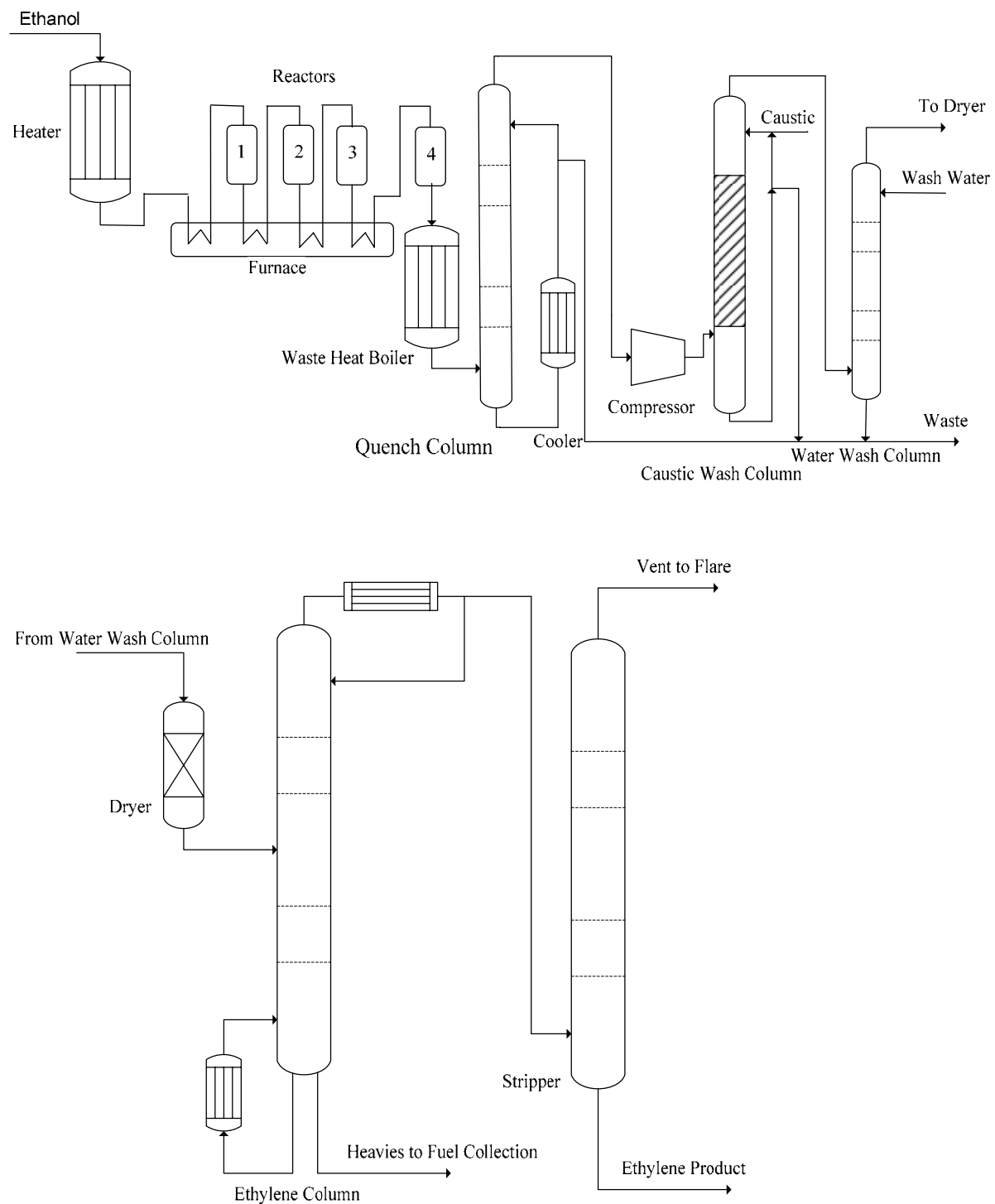
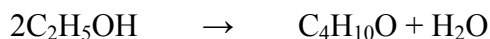Figure 2.1: Process Flow Diagram of Ethanol based Ethylene Production.

bottom products from the ethylene column (containing heavier by-products) can be used as fuel in the furnace reducing the need for external fuel. The bottom product from the stripper satisfies the product specifications for polymer grade ethylene (i.e. 99.95 vol%).

2.3.1 Reactor

The reactor is the most important unit in the ethanol dehydration to ethylene process. It is where the conversion of ethanol to ethylene occurs. High ethanol conversion (up to 99 %) and high selectivity towards ethylene (94.5-99%) is achieved by using syndol catalyst which is a very stable high yield ethanol dehydration catalyst.

2.3.1.1   Catalytic Reactions

Ethylene from ethanol dehydration is a catalytic endothermic reaction. Chematur uses a SynDol, i.e. aluminum-oxide, catalyst developed by Halcon SD. Ethylene (C_2H_4) formation is predominant in temperature regions of 320°C – 500°C, while in temperature regions of 150°C – 300°C the formation of diethylether ($C_4H_{10}O$) is predominant. Consequently, the operating conditions in the reactor are of utmost importance to achieve high selectivity towards ethylene.

$$C_2H_5OH \quad \rightarrow \quad C_2H_4 + H_2O \qquad\qquad \Delta H = +390 \text{ Kcal/Kg of ethylene}$$

$$2C_2H_5OH \quad \rightarrow \quad C_4H_{10}O + H_2O$$

Ethylene can also be formed with diethylether as an intermediate. This makes the contact time with the catalyst an important parameter in order to achieve the desired product, i.e. ethylene. Additional reactions occurring during ethanol dehydration are the formation of byproducts, such as propene (C_3H_6), butylene (C_4H_8), ethane (C_2H_6), carbon monoxide (CO) and carbon dioxide (CO_2). High ethanol conversion (up to 99.9%) and high selectivity towards ethylene (94.5-99%) can be achieved operating at the right reactor conditions.

2.3.1.2   Adiabatic versus Isothermal Reactors

The ethanol dehydration reaction is endothermic and the product formation is highly temperature dependent. Therefore the operating temperature is required to be kept in a certain range in order

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to govern the selectivity towards ethylene. This can be achieved with either adiabatic or isothermal reactors.

Isothermal reactors operate with a circulating heating fluid outside the reactor supplying heat and maintaining the temperature in the reactor. Commercial heating fluids have a maximum working temperature of approximately 370°C, due to thermal decomposition. As a consequence the reactor is limited to relatively low operating temperatures, resulting in reduced ethanol conversion and ethylene selectivity. To provide sufficient heat to the reactor, i.e. maintain the temperature, the area is increased by introducing a tube-package. The large number of tubes will increase the capital cost for the reactor.

Operating with adiabatic reactors, the heating fluid outside the tubes is avoided. This will enable operating temperatures above 370°C. Thus the reactor inlet temperature can reach temperature regions of 450°C – 500°C. The reactor can consist of one reactor or several in series or in parallel. The process used by Chematur International AB uses four tubular adiabatic reactors connected in series. Since the reaction is endothermic the effluent from each reactor requires reheating before entering the subsequent reactor. If the temperature is kept within an appropriate range, high ethanol conversion and high ethylene selectivity will be obtained. Additionally, higher selectivity towards ethylene results in lower production of by-products which require removal downstream in the process in several purification steps. The capital cost for adiabatic reactors is comparatively lower than for isothermal reactors.

2.3.1.3   Reactors Operating Conditions

The operating conditions of the reactor e.g., effect of operating temperature, effect of operating pressure and concentration of the feed have a significant effect on obtained conversion and selectivity.

As already mentioned operating temperature has a significant effect on the ethylene yield. Adequate operating temperature (isothermal reactor) and inlet temperature (adiabatic reactor) to maintain high conversion and selectivity in/throughout the reactor is important. Ethanol conversion and ethylene selectivity decreases with increasing pressure. The effect is stronger in lower temperature regions.

In the reactor, temperature rise has a positive effect on conversion and selectivity in temperature regions above 375°C. In an adiabatic reactor, the temperature gradient is lesser. As a result the amount of catalyst required is reduced and the formation of by-products (such as diethylether) is reduced. Additionally a lower frequency of catalyst regeneration is required due to less coke formation and the catalyst lifetime increases.

2.3.2 Furnace

A furnace provides sufficient heat to the reactor(s) to enable desired operating temperature.

2.3.3 Quench Tower

In the quench tower, water present in the reactor effluent stream is condensed by cooling the entering gas with spray water from the top of the tower. The liquid, in the bottom of the tower contains condensed water, impurities, and unconverted ethanol. A fraction of the bottom product is cooled and recirculated back as spray-water, while the remainder is sent to the wastewater treatment.

2.3.4 Compressor

The gas stream leaving the quench tower mainly consists of ethylene. In order to enable sufficient pressure through downstream units the gas is compressed in a multi-stage compressor. Between each compressor stage an intercooler and a knockout drum is placed, removing some of the remaining water. Literature states outlet pressures from the last compressor between 20-29 bar. The outlet pressure is set to obtain desirable operating temperature in the downstream ethylene column condenser.

2.3.5 Caustic Tower

In the caustic tower CO_2 is absorbed by washing the gas with sodium hydroxide (NaOH) in a packed column. The final ethylene product needs to fulfill the product specification of maximum 10 vol-ppm CO_2 in order to enable polymerization. On top of the caustic tower a water wash is placed spraying water on the gas. As a result the sodium hydroxide is washed out.

2.3.6 Dryer

The remaining water is removed in a dryer. The incoming gas is first cooled prior entering a molecular sieve. The gas leaving the dryer contains zero or close to zero moles of water.

2.3.7 Ethylene Column and Stripper

After the dryer, heavier impurities are removed in a distillation column. The ethylene column, also referred to as the C_2-splitter, essentially separates ethane from ethylene. The light key component is ethylene and the heavy key component is ethane. The operating temperature for the column is restricted by available cooling medium.

The bottom product consists of ethanol, diethylether, and acetaldehyde, which e.g. can be used as fuel. The condenser serves as a joint condenser for both ethylene column and stripper. In the stripper carbon monoxide (CO), methane (CH_4), and hydrogen (H_2) are separated from ethylene. To minimize ethylene losses the top product of the stripper is sent to the joint condenser. In the condenser the light by-products separated in the stripper is vented to air while the condensed phase (containing mainly ethylene) is recirculated to ethylene column and stripper.

The final ethylene product has to meet certain purity specifications prior to polymerization, i.e. it must be of polymer grade (which means having a purity of 99.85 – 99.95 vol% ethylene. Acceptable impurity levels are shown in Table 2.1. This requirement must be achieved in order to obtain desirable product qualities and also because the PE-catalyst is oxygen sensitive.

Components	Composition
Ethylene (vol %)	99.95
Carbon Monoxide (vol ppm)	5
Carbon Dioxide (vol ppm)	10
Ethane (vol %)	0.05

Table 2.1: Polymer grade ethylene.

2.4 Cost Estimation of Ethanol Based Ethylene Production

Total capital investment for ethanol based ethylene production plant designed to produce 30 metric ton/day of ethylene (having a purity of 99.95 vol %) as shown in Figure 2.1 has been estimated [9, 10].

2.4.1 Purchased Cost of Equipments

The cost of purchased equipment is the basis of several predesign methods for estimating capital investment. Sources of equipment prices, methods of adjusting equipment prices for capacity and methods of estimating auxiliary process equipment are therefore essential to the estimator in making reliable cost estimates.

Purchased cost of major equipment items for ethanol based ethylene production plant is estimated and is given in Table 2.2.

S. No.	Equipments	Specifications	Cost in US$
1	Pre-heater	Heat transfer area $= 2.06 \text{ m}^2$	2000
2	Heat exchanger	Heat transfer area $= 51.92 \text{ m}^2$	8000
3	Reactor (four reactors in series)	L = 4.7 m, D = 1.5 m	57600
4	Waste heat boiler	Heat transfer area $= 76.9 \text{ m}^2$	10000
5	Quench column	L = 12.8 m, D = 1.5 m	5600
6	Cooler	Heat transfer area $= 1.45 \text{ m}^2$	1800
7	Compressor	Two-stages, reciprocating	15000
8	Caustic wash column	L = 5.52 m, D = 1.5 m	22400
9	Water wash column	L = 1.8 m, D = 1.5 m	11200
10	Dryer	L = 2.7 m, D = 1 m	6400
11	Ethylene column	L = 21.94 m, D = 2 m	13440

12	Stripper	L = 18.2 m, D = 2 m	11200
Total purchased equipment cost (year 2004)			**164640 $**

Table 2.2 Purchased Cost of Ethanol Based Ethylene Production Plant.

Chemical engineering cost index in 2004   =   444.2

Chemical engineering cost index in 2009   =   575.4

Now, by using following equation,

$$\text{Puchased equipments cost in US\$} = \text{Cost in 2004} \times \frac{\text{cost index in 2009}}{\text{cost index in 2004}}$$

Purchased equipment cost ($)   =   213268.47 $

2.4.2 Direct Cost

a. Purchased equipment cost (PEC)   =   213268.47 $

b. Purchase Equipment Installation (47% of a)   =   100236.18 $

c. Instrumentation and control (36% of a)   =   76776.65 $

d. Piping Cost (68% of a)   =   145022.56 $

e. Electrical Systems (11% of a)   =   23459.53 $

f. Building (18% of a)   =   38388.32 $

g. Yard Improvement (10% of a)   =   21326.84 $

h. Service Facility (70% of a)   =   149287.93 $

A. Total direct cost (a+b+c+d+e+f+g+h)   =   767766.50 $

2.4.3 Indirect Cost

i. Engineering and Supervision (33% of a)   =   70378.59 $

j. Construction expenses (41% of a)   =   87440.07 $

k. Legal Expenses (4% of a)   =   8530.73 $

l. Contractor's Fee (22% of a)   =   46919.06 $

m. Contigency (44% of a)   =   93838.12 $

B. Total indirect cost (i+j+k+l+m)   =   307106.60 $

2.4.4 Total Fixed Capital Investment

Total fixed capital investment is the sum of direct cost and indirect cost

C. Total fixed capital investment (A+B)   =   1074873.10 $

2.4.5 Working Capital

D. Working capital (89% of a)   =   189808.94 $

2.4.6 Total Capital Investment

Total capital investment is the sum of fixed capital investment and working capital

E. Total capital investment (C+D)   =   1264682.04 $ = 1.26 million $

2.4.7 Production Cost

2.4.7.1   Variable Production Cost

n. Raw material (ethanol)   =   12570033.6 $

o. Fuel oil   =   596160 $

p. Steam   =   36914.22 $

q. Cooling water   =   2221.8 $

r. Operating labor   =   490590 $

s. Operating supervision (15 % of r)   =   73588.5 $

t. Maintenance and repair (7 % of C)   =   75241.11 $

u. Operating supplies (15 % of t)   =   11286.16 $

v. Laboratory charges (15 % of r)   =   73588.5 $

F. Total variable production cost (n+o+p+q+r+s+t+u+v) =   13929623.91 $

2.4.7.2   Fixed Production Cost

w. Taxes (2 % of C)   =   21497.46 $

x. Insurance (1 % of C)   =   10748.73 $

y. Depreciation [(a + f)/20]   =   12582.83 $

G. Total Fixed Production Cost (w+x+y)   =   44829.03 $

H. Plant Overhead (50 % of r)   =   245295 $

Total Production Cost = Variable production cost + fixed production cost + plant overhead

So, Total annual production cost (F+G+H)   =   14219747.94 $ = 1.42 million $

Annual production   =   10950 ton/year

Production Cost per unit of ethylene   =   1298.60 $/ton = 1.29 $/Kg of
ethylene

2.5   Cost Comparison

Cost Components	Naphtha based ethylene production (30 ton/day)	Ethanol based ethylene production (30 ton/day)
Purchased equipment cost ($)	291715.62	213268.47
Direct cost ($)	1050176.24	767766.50
Indirect cost ($)	420070.49	307106.60
Fixed capital investment ($)	1470246.74	1074873.10
Working capital ($)	259626.90	189808.94

Total capital investment ($)	1729873.64 (1.72 million $)	1264682.04 $ (1.26 million $)
Total Annual Production Cost	16121972.29$ (1.61 million $)	14219747.94$ (1.42 million $)
Cost per unit of ethylene	1472.32 $/ton = 1.47 $/Kg	1298.60 $/ton = 1.29 $/Kg

Table 2.4: Cost Comparison of Ethylene Production from Ethanol and Naphtha.

Chapter 3

Process Selection & Description

3.1   Process Selection: Ethylene from Dehydration of Ethanol

Ethylene produced form ethanol has attracted more and more attention in comparison with the way from steam cracking of petroleum or natural gas feed stock. In recent years, with the shortage of natural resource and energy, the way of ethanol dehydration into ethylene over a catalyst has attracted more attention compared with the traditional route because of some advantages, such as the reduction of CO_2, low production cost and energy consumption.

And secondly plenty of ethanol can be produced from molasses (a by-product of sugar industry). It undergoes fermentation in the presence of enzymes present in yeast to give ethanol. Many local sugar mills in Pakistan are converting this molasses into ethanol. The alcohol does not have market as a drink in country like Pakistan; therefore, it can be converted into ethylene for its onward conversion into polyethylene because the petroleum route for this polymer has gone more expensive.

A techno-economic analysis of production of 30 ton/day of ethylene from dehydration of ethanol and from thermal cracking of naphtha for the same plant capacity is performed which clearly shows that the cost of ethanol based ethylene production plant is lower than that from naphtha cracker for the same ethylene production and purity.

Due to the above mentioned reasons, the dehydration of ethanol is preferred for the production of ethylene.

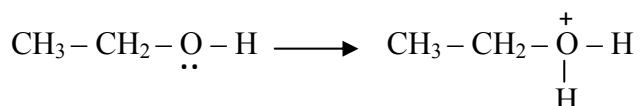## 3.2   Dehydration of Ethanol

In the present study, the attention was focused on the catalytic conversion of ethanol into ethylene. The chemistry of ethylene production via dehydration of ethanol can be presented by the following reaction.

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O$$

$$2C_2H_5OH \longrightarrow C_4H_{10}O + H_2O \text{ (side reaction)}$$
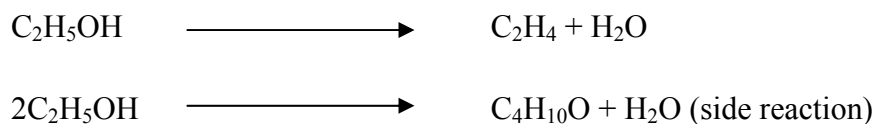
The dehydration reaction is carried out at 315-425 ^oC (599-797 ^oF) over alumina catalyst in a fixed bed reactor. The ethylene is obtained in high purity yields. A conventional purification scheme may be used to remove any trace by-product [11].
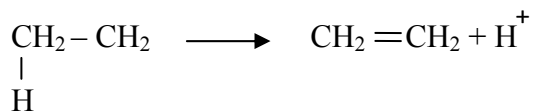
3.3   Reaction Mechanism and Kinetics

In the first stage, one of the lone pairs of electrons on the oxygen picks up a hydrogen ion. The alcohol is said to be protonated.

$$CH_3 - CH_2 - \overset{..}{\underset{..}{O}} - H \longrightarrow CH_3 - CH_2 - \overset{+}{O} - H$$
$$\underset{\underset{H}{|}}{}$$

The protonated ethanol loses a water molecule to give a carbocation (a carbonium ion).

$$CH_3 - CH_2 - \overset{+}{O} - H \longrightarrow CH_3 - \overset{+}{CH_2} + H_2O$$
$$\underset{\underset{H}{|}}{}$$
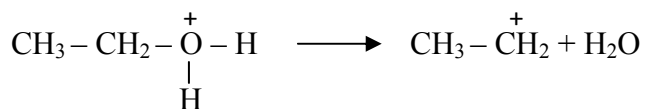
Finally, a hydrogen ion from the carbocation is pulled off.

$$CH_2 - CH_2 \longrightarrow CH_2 = CH_2 + H^+$$
$$\underset{\underset{H}{|}}{}$$

Production of ethylene via dehydration of ethanol is temperature sensitive process. Formation of ethylene is favored by high temperature however at some lower temperature diethyl ether can be produced as by product.

The dehydration of ethanol at different temperatures and partial pressure of ethanol has been studied and it is stated that the rate of ethylene formation is independent of partial pressure of ethanol and could be considered as zero order reaction. The effect of temperature on the reaction is that, for every 10 ^oC rise in the reaction temperature, the rate is doubled. The activation energy for ethylene formation is 45.8 kcal/mol [12].

The reaction is endothermic requiring about 390 kcal per kg of ethylene produced. In addition, the reaction is reversible with the equilibrium being favored by high temperature and hindered by the presence of water vapor in the feed. The recovery of unconverted ethanol for recycling is

energy and capital intensive and reaction conditions enabling maximum conversion of ethanol are usually preferred [11].

3.4   Process Description

Process flow diagram is show in Figure 3.1. Ethanol feed is taken in a 10 liters vessel made of stainless steel. Inside the vessel, an electric heater of 6 KW is installed which is used to heat ethanol upto 100 ^{o}C. At this temperature liquid ethanol is converted into ethanol vapors. On the process line, there is a needle valve and gas rotameter to control and measure the flow rate of ethanol vapors. These ethanol vapors are passed through a fixed bed reactor (made of stainless steel) filled with alumina catalyst and the rest of the reaction temperature is achieved in the fixed bed reactor which is heated externally by electric heating tape, wrapped around the reactor across the whole length to eliminate hot and cold spot because in this case the reaction temperature is a critical operating parameter: excessive temperature produces aldehydes and low temperature produces ether.

So in this experimental study, the desired reaction temperature is achieved by two stages heating just for the sake of safety and easy handling of the whole experimental rig. However the ethanol feed vessel is equipped with pressure relief valve (safety valve) to avoid any excessive pressure build-up in the ethanol feed vessel. A compound pressure gauge is installed on the top of this vessel to read the pressure of ethanol vapors inside the vessel.

Ethanol is converted into ethylene as it passes through fixed bed reactor filled with alumina catalyst at required reaction temperature. The reactor effluent is collected in a solvent that dissolves maximum of ethylene gas produced. The reaction products are then analyzed by certain confirmatory tests.
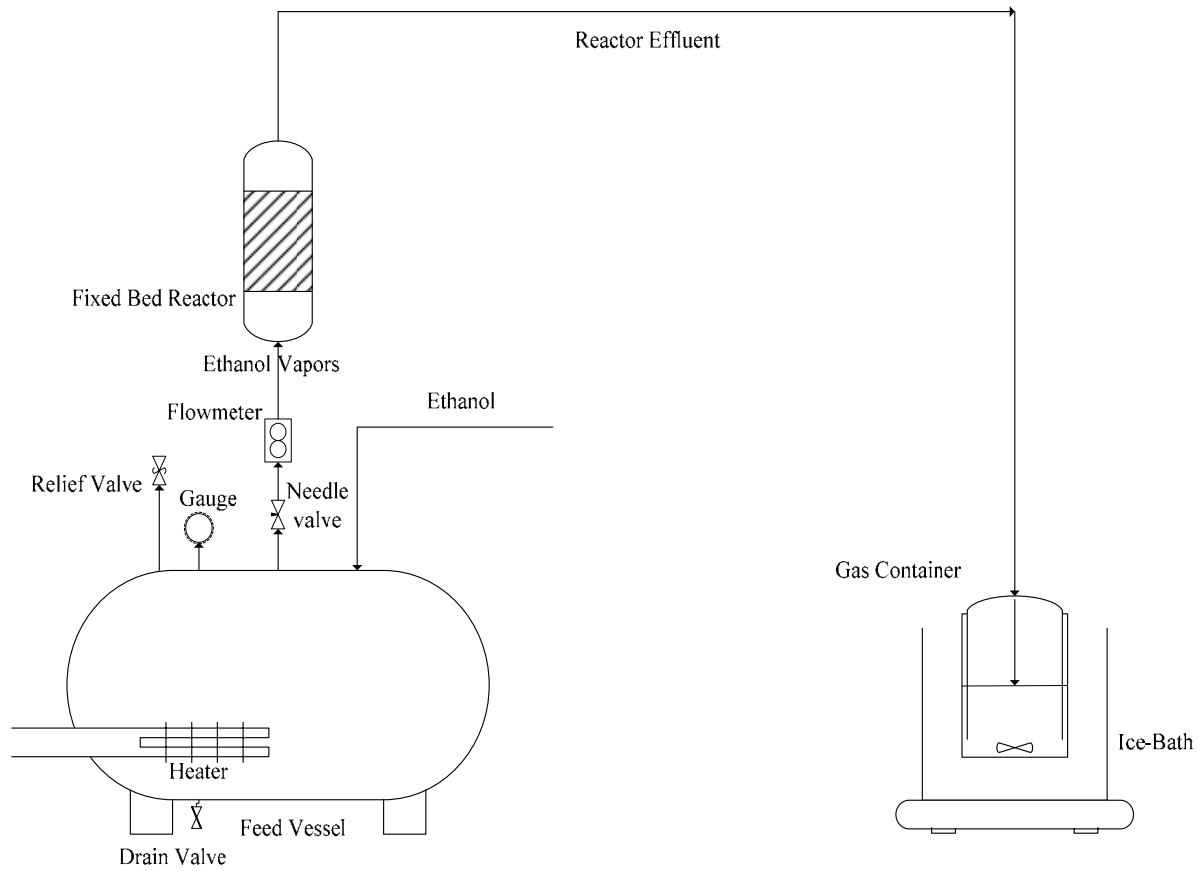
Figure 3.1: Process Flow Diagram of Ethylene Production through Dehydration of Ethanol.

Chapter 4

Reactor Design

4.1   Introduction

This chapter covers the design and development of laboratory experimental rig. The experimental rig is a small scale unit capable to carry out the dehydration of ethanol over alumina catalyst at the desired reaction temperature and pressure.

Figure 4.1: Experimental Rig for Dehydration of Ethanol.

4.2   Parts of Experimental Rig

Laboratory experimental rig comprises of following main components

- Feed vessel

- Electric heater

- Drain valve

- Needle valve

- Compound pressure gauge

- Pressure relief valve

- Gas flow meter

- Fixed bed reactor

- Heating tape

- Gas container

- Control panel

- Stand for rig

4.3   Fixed Bed Reactor

Fixed bed reactors are used in chemical reactions. These reactors are tubular and are filled with solid catalyst particles, most often used to catalyze gas reactions. In these types of reactors, the catalyst pellets are held in space with respect to a fixed reference frame and the chemical reaction takes place on the surface of the catalyst. There are two basic types of packed bed reactor; those in which the solid is a reactant and those in which the solid is a catalyst.

In chemical process industries, the emphasize is mainly on the designing of catalytic reactors. Industrial packed bed catalytic reactors range in size from small tubes, a few centimeters

diameter to large diameter packed beds. Packed-bed reactors are used for gas, gas-solid and gas-liquid reactions. Heat-transfer rates in large diameter packed beds are poor therefore, where high heat-transfer rates are required, fluidized beds should be considered.
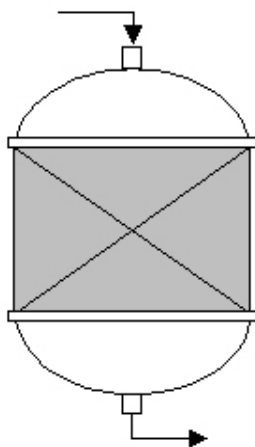

Figure 4.2: Fixed Bed Reactor.

There are many types of reactors available to carry out chemical reactions Each type of reactor has its own advantages and disadvantages depending upon the type of reactions and reaction condition. Some advantages and disadvantages of fixed bed reactor is given in following table.

Type of Reactor	Characteristics
Tubular fixed bed Reactor	Tubular reactor that is packed with solid catalyst particles.

Kinds of Phases Present	Usage	Advantages	Disadvantages
1. Gas phase/ solid catalyzed	1. Used primarily in heterogeneous phase reactions with a catalyst	1. High conversion per unit mass of catalyst	1. Undesired thermal gradients may exist

2. Gas-solid reactions		2. Low operating cost	2. Poor temperature control
		3. Continuous OPeration	3. Channeling may occur
		4. Simple as compared to fluidized bed	4. Unit may be difficult to service and clean

Since the reaction occurs in gaseous phase catalyzed by solid particle and because of low operating cost and simple design, fixed bed reactor is selected for the dehydration of ethanol to produce ethylene gas.

4.4 Design of Fixed Bed Reactor

Chemical Reaction

$$C_2H_5OH \xrightarrow[\substack{315\text{-}425\ ^oC \\ 1\ atm}]{\text{Aluminium Oxide}} C_2H_4 + H_2O$$
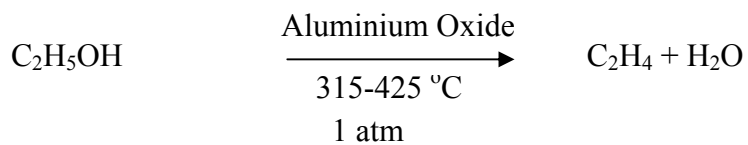
Catalyst

Catalyst used for the dehydration of ethanol is alumina.

Reaction Conditions

Temperature	:	315-425 ^oC
Pressure	:	1 atm
Residence Time	:	2 s

4.4.1 Material Balance across Reactor

Basis: 1 Liter of feed (ethanol)

The dehydration reaction is governed by the following equations

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O$$
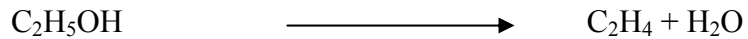
Volume of ethanol = 1 L

Density of ethanol = 0.789 kg/L

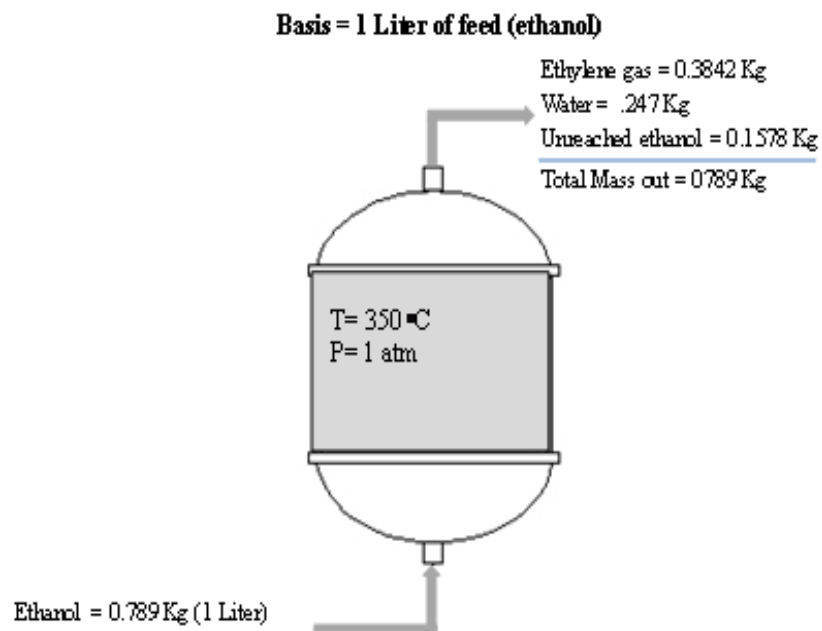Mass of ethanol = density x volume = 0.789 Kg

By Assuming 80 % conversion, mass of reacted ethanol = 0.6312 Kg

Mass of unreacted ethanol = 0.1578 Kg

According to reaction equation,

Ethylene produced = 0.3842 Kg

Water produced = 0.247 kg

Basis = 1 Liter of feed (ethanol)

Ethylene gas = 0.3842 Kg
Water = .247 Kg
Unreached ethanol = 0.1578 Kg
Total Mass out = 0789 Kg

T= 350 C
P= 1 atm

Ethanol = 0.789 Kg (1 Liter)

Material in	=	Material Out
0.789 Kg		Ethylene = 0.3842 Kg
		Water = .247 Kg
		Unreacted Ethanol = 0.1578 Kg
Total Material In = 0.789 Kg	=	Total Material Out= 0.789 Kg

4.4.2 Heat Requirements

Heating is done in two stages

a. With the help of electric heater in feed vessel

Inlet temperature of ethanol = 25 ^{o}C

Outlet temperature of ethanol = 100 ^{o}C

Average temperature of ethanol = 62.5 ^{o}C

Cp of ethanol at average temperature = 112.4 J/mol.k = 2.44 J/g. ^{o}C

Volume of ethanol in feed vessel = 8 L

Density of ethanol = 0.789 Kg/L

Mass of ethanol = density x volume = 6.312 Kg = 6312 g

Heat duty = Q = m.Cp.ΔT = 15401.28 J

Let time required for heating ethanol from 25 ^{o}C to 100 ^{o}C in feed vessel = 5 min = 300 s

Then Q = 51.33 J/s

b. With the help of heating tape wrapped around reactor

Inlet temperature of ethanol vapors = 100 ^{o}C

Outlet temperature of ethanol vapors =   400 ^{o}C

Average temperature of ethanol vapors = 250 ^{o}C

Cp of ethanol vapors at average temperature = 87.53 J/mol.k = 1.9 J/g. °C

Volumetric flow rate of ethanol vapors = 2 L/min

Density of ethanol vapors = 0.0015 g/ml

Mass flow rate of ethanol = m = 0.05 g/s

Heat duty = Q = m.Cp.ΔT = 28.5 J/s

4.4.3 Dimensions of Reactor

Basis: 2 Liters/min of ethanol vapors

Volumetric flow rate of ethanol vapors = 2 L/min = 3.33 x 10^{-5} m^3/s

Residence time = 2 s

Volume of catalyst = volumetric flow rate of feed x residence time = 6.66 x 10^{-5} m^3

Particle density of alumina catalyst = 1.13 g/cm^3 = 1.13 Kg/L = 1130 Kg/m^3

Weight of catalyst = particle density x volume of catalyst = 0.753 Kg = 75.3 g

Volume of reactor = volume of catalyst (1+ ø) = 9.33 x 10^{-5} m^3 = 0.0933 L

Where ø = Void Fraction = 0.4

Add 25% of volume of reactor for gas space and fitting

Now volume of reactor = V = 9.33 x 10^{-5} x 1.25 = 1.166 x 10^{-4} m^3 = 0.1166 L

To find length and diameter of reactor,

Assume L/D = 7

Where,

L = Length of reactor

D = Diameter of reactor

Volume of reactor = V= π/4 x D^2 = 1.166 x 10^{-4} m^3

By putting D = L/7, L = 0.1938 m = 0.6358 ft = 7.6 inch

D = L/7 = 0.0276 m = 0.0905 ft = 1 inch

So,

Length of reactor = L = 0.1938 m

Diameter of reactor = D = 0.0276 m

4.4.4 Specification Sheet

Equipment	Reactor
Type	Catalytic fixed bed
Function	Dehydration of ethanol
Catalyst	Alumina
Operating temperature	315-425 ^{o}C
Operating pressure	1 atm
Volume	0.1166 L
Length	0.1938 m
Diameter	0.0276 m
Material of construction	Stainless steel

Table 4.1: Specification of fixed bed reactor.

Chapter 5

Experimental Work

5.1   Installation and Inspection

After installation of all the components of experimental rig in the laboratory, the feed vessel is filled with water and switched on the electric heater on control panel and gave the set point at 100 ^{o}C. At 100 ^{o}C, water starts to boil. So when the temperature of water inside the feed vessel reached 100 ^{o}C, The needle valve is opened gradually and allowed water vapors to pass through the flow meter and then through process line. The purpose of this run is just to check any leakage present in the process line from feed vessel to final product collector.

And during this test run, safety limit of pressure relief valve is set at 5 bar and kept the fixed bed reactor unfilled with catalyst and also checked the temperature of heating tape that is wrapped around the fixed bed reactor by switching on the heating tape on control panel and setting the temperature upto a range of 300 – 400 ^{o}C.

5.2   Experimental Procedure

After the inspection of laboratory experimental rig with water, fixed bed reactor is filled with the alumina catalyst and then fitted it according to the process flow diagram as shown in Figure 3.1. Then filled the feed vessel with ethanol upto the required level and switched on the electric heater on control panel and set the temperature at 100 ^{o}C. Initially ethanol is fed to the feed vessel at ambient temperature so it took some time to heat the ethanol from ambient temperature to 100 ^{o}C. Meanwhile switched on the heating tape that is wrapped around the fixed bed reactor and set the temperature at 350 ^{o}C.

Since the boiling point of ethanol is 78 ^{o}C so ethanol in the feed vessel is converted into vapors when the set point is reached.

When the temperature of electric heater reached upto 100 ^{o}C and the temperature of heating tape reached upto 350 ^{o}C, opened the needle valve gradually and adjusted the flowrate of ethanol vapors with the help of gas flow meter.

So after achieving reaction conditions, the vapors of ethanol are passed over alumina catalyst in the fixed bed reactor. Reaction occurred and ethanol is converted into reaction products.

After that, sampling bottle is taken and evacuated it with the help of vacuum pump and connected it to the line at exit of the fixed bed reactor and collected a sample of product gas to perform necessary confirmatory tests.

5.3   Confirmatory Tests

Two common types of unsaturated compounds are alkenes and alkynes, characterized by the carbon-carbon double and triple bond, respectively, as the functional group. There are no simple direct ways to prepare solid derivatives of unsaturated aliphatic compounds having no other functional groups. Two common qualitative tests for unsaturation are the reaction of the compounds with bromine in carbon tetrachloride or water and with potassium permanganate. In both cases a positive test is denoted by decolorization of the reagent.

5.3.1 Bromine Water Test

Bromine will add to the carbon-carbon double bond of alkenes to produce dibromoalkanes. When this reaction occurs, molecular bromine is consumed, and its characteristic dark red-brown color disappears if bromine is not added in excess. The rapid disappearance of the bromine color is a positive test for unsaturation.

Experimental Procedure:

1) A dilute solution of bromine has been prepared in water and then set at least three test tube in a test tube rack in the hood.

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2) Added bromine water in these three test tubes.

3) Then added collected ethylene gas sample (dissolved in water) into these test tubes.

4) The bromine reagent is brown or yellow brown in color and observed each test tube for the dissipation of brownish color.

Result

The dissipation of brownish color in every test tubes indicates that the tested gas is unsaturated i.e. ethylene.

5.3.2 Baeyer Test

A second qualitative test for unsaturation, the Baeyer test, depends on the ability of potassium permanganate to oxidize the carbon-carbon double bond to give alkanediols.
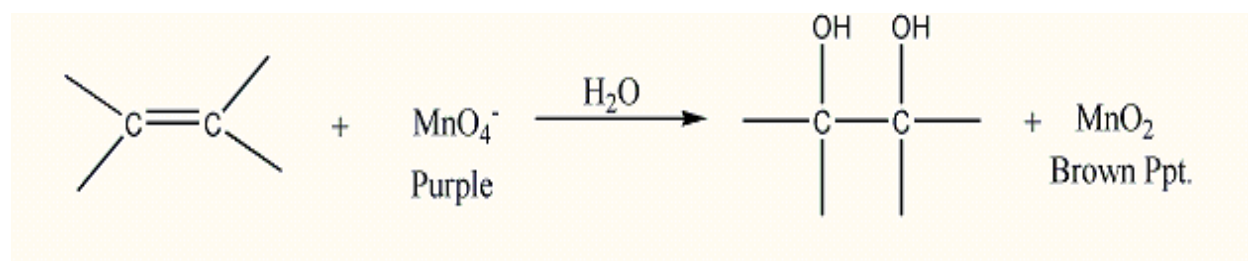
The permanganate is destroyed in the reaction, and a brown precipitate of MnO_2 is produced. The disappearance of the characteristic color of the permanganate ion is a positive test for unsaturation. However, care must be taken, since compounds containing certain other types of functional groups (for example, aldehydes, containing the --CH=O group) also decolorize permanganate ion.

Experimental Procedure

1) A dilute solution of potassium permanganate has been prepared in water and then set at least three test tube in a test tube rack in the hood.

2) Added potassium permanganate solution in these three test tubes.

3) Then added collected ethylene gas sample (dissolved in water) into these test tubes and observed the color change.

Result

The disappearance of the purple color and the appearance of a brown suspension is a positive test.

Chapter 6

Result & Discussion

6.1   Result and Discussion

Two confirmatory tests are performed in the laboratory for the presence of ethylene i.e. Bromine water test and Baeyer test.

In Bromine water test, the dissipation of the brown color of bromine reagents indicated that tested product contained an unsaturated hydrocarbons, ethylene

Similarly in Bayer test the dissipation of the purple color of potassium permanganate and the appearance of a brown suspension due to the formation of manganese dioxide indicated that tested product is an unsaturated hydrocarbons, ethylene.

Although the findings observed in the present study are greatly attracted, further investigation by the gas chromatographic technique is necessary for clarifying the more details regarding products formation and their compositions.

6.2   Conclusion

An experimental rig to carry out the dehydration of ethanol is designed, fabricated and tested. Ethylene is obtained by the dehydration of ethanol over alumina catalyst in a fixed bed reactor. This method of ethylene production from ethanol may open a new pathway for the production of a number of petrochemicals from a non-petroleum feedstock, namely ethanol. Results obtained from ethylene confirmatory test showed the confirmation of ethylene.

6.3   Future Recommendations

It is observed that the following items should be added in the present experimental rig for the calculations of percent conversion of ethanol (feed) and yield of the product.

6.3.1 Compressor

A compressor should be needed which can transfer the reactor effluent to the gas container or gas storage vessel.

6.3.2 Gas Storage Assembly

A gas storage tank or gas container is needed which can store sufficient quantity of reactor effluents and it should be equipped with temperature sensor and pressure sensor.

6.3.3 Sampler

A sampler must be needed which should be capable to collect a sample of reactor effluent from the line at the outlet of rector or from gas storage tank for qualitative and quantitative analysis of the product stream by gas chromatographic technique.

References

1) Ethylene by Heinz Zimmermann, Linde AG, Hoellriegelskreuth, Federal Republic of Germany and Roland Walzl, Linde AG, Hoellriegelskreuth, Federal Republic of Germany.

2) http://en.wikipedia.org/wiki/Ethylene

3) "A report on ethylene" by K. M. Sundaram, M. M. Shreehan, and E. F. Olzewsk, ABB Lummus Global.

4) http://www.icis.com/v2/chemicals/9075777/ethylene/uses.html

5) "Ethylene: Product Stewardship Guidance Manual" Published by American Chemistry Council (CHEMSTAR), December, 2004.

6) "Steam Cracking of Naphtha in Packed Bed Reactors" by Jafar Towfighi, Heinz Zimmermann, Ramin Karimzadeh, and Mohammad M. Akbarnejad, Chemical Engineering Department, Tarbiat Modarres University, Tehran, Iran.

7) "Olefins from Conventional and Heavy Feedstocks: Energy use in Steam Cracking and Alternative Processes" by Tao Ren, Martin Patel, Kornelis Blok, Department of Science, Technology and Society, Faculty of Chemistry, Utrecht University, Netherland.

8) "The Combined Simulation of Heat Transfer and Pyrolysis Reactions in Industrial Cracking Furnaces" by A. Niaei, J. Towfighi, S. M. Sadrameli, and R. Karimzadeh, Chemical Engineering Department, Tarbiat, Modarres University, Tehran, Iran.

9) Max S.Peters, Klaus D.Timmerhaus and Ronald E.West, "Plant Design and Economics for chemical Engineers", 5th Ed, McGraw Hill International Book Company, London. Mexico. New Delhi. Singapor. Tokyo.

10) Coulson, J.m., and Richardson, J.F., "Chemical Engineering", 2nd Ed, Vol-6, Butterworth Heminann.

11) "Workshop and Report on Implications of Bio-refineries for Energy and Trade in the APEC Region (EWG 05/2008A)" by Nexant, Inc. and Industrial Technology Research Institute (ITRI), China.

12) "Mechanism of Dehydration of Ethanol over Alumina" by Fikry M. Ebeid, Department of Chemistry, Faculty od Science, Qatar University, Doha, Qatar.