Conversion of Ethanol to Ethylene

By

Ayesha Tanweer	**00000133852**
M. Shahadat Awan	**00000139270**
M. Sohair Abid	**00000147402**

School of Chemical and Materials Engineering (SCME)

National University of Sciences and Technology (NUST)

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Ayesha Tanweer	00000133852
M. Shahadat Awan	00000139270
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Supervisor: Dr. Sarah Farrukh

Co-Supervisor: Dr. Erum Pervaiz

School of Chemical and Materials Engineering (SCME)

National University of Sciences and Technology (NUST)

H-12 Islamabad, Pakistan

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Certificate

This is to certify that work in this thesis has been carried out by **Ms. Ayesha Tanweer, Mr. Shahadat Awan** and **Mr. Sohair Abid** completed under my supervision in School of Chemical and Materials Engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan.

Supervisor:________________

Dr. Sarah Farrukh

Assistant Professor

Chemical Engineering Department

School of Chemical & Materials

Engineering (SCME)

National University of Sciences and

Technology (NUST), Islamabad

Co Supervisor:________________

Dr. Erum Pervaiz

Assistant Professor

Chemical Engineering Department

School of Chemical & Materials

Engineering (SCME)

National University of Sciences and

Technology (NUST), Islamabad

Submitted through:

HoD:______________________

Dr. Muhammad Bilal Khan Niazi

Chemical Engineering Department
School of Chemical & Materials
Engineering (SCME)
National University of Sciences and
Technology, Islamabad

Principal/ Dean: _______________

Dr. Arshad Hussain

Chemical Engineering Department
School of Chemical & Materials
Engineering (SCME)
National University of Sciences and
Technology, Islamabad

Dedication

To SCME, our beloved parents, teachers and friends without whose continual support, this could not have been achieved.

Acknowledgement

All thanks to **Allah Almighty** for His countless blessings and rewards, who gave us the strength and ability to complete this thesis.

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Abstract

Being a raw material for 75% of the petrochemicals, Ethylene is considered as the bedrock of chemical industry. Although its demand is increasing day by day, yet there is no industry in Pakistan producing Ethylene and all the needs are met by relying on imports.

All Ethene manufacture processes which are being implemented across the globe have been compared in detail. After considering Pakistan's self-sufficiency in terms of raw material, as well as other factors such as eco-friendliness and energy efficiency, the process of Ethanol dehydration has been finalized.

For implementing the process Nano-CAT (a modified HZSM-5 zeolite) has been utilized at a low pressure of 1.5 atm giving high conversions of ethanol (99.2%) with a very high ethylene selectivity (98.69%), at a considerably lower temperature of $240℃$. Nano-CAT produces no CO_2 and very low amounts of CO, thereby eliminating the needs of CO_2 absorber and C2 splitter respectively, to cut down on the overall equipment cost. The process has been successful in achieving the required polymer grade purity of ethene (99.9%)

Overall the process thus presents a sustainable, environment friendly and energy efficient pathway to meet the ever-increasing demands of Ethylene. The report then includes a detailed process flow diagram, material and energy balance, equipment design, instrumentation, simulation, economic analysis and HAZOP analysis of the whole plant.

1 Introduction

The target of this project - Ethylene - is one of the main and most important chemicals in the world and is the raw material for about 75% of the products of petrochemical industry such as acetaldehyde, acetic acid, ethylene oxide, ethylene glycol, ethylbenzene, chloroethanol, vinyl chloride, styrene, ethylene dichloride, and vinyl acetate, etc. It is also used as a polymerization raw material for a large range of important organic chemical products such as polyethylene, polyvinyl chloride, polystyrene etc. (Minhua Zhang, 2013)

Production of Ethylene is seen as a direct measure of the petrochemical development of a country, all around the world. A number of different processes have been used over the past years for the production of Ethylene. Our main objective is to utilize the most suitable process according to Pakistan’s requirements and situation.

1.1 Ethylene

Ethylene is the smallest alkene having the chemical formula C_2H_4. It is a colourless flammable gas at room temperature.

1.1.1 General Chemical Properties

- It has a chemical formula C_2H_4
- It has an average molecular weight of 28 g/mol
- It has a slightly sweet musky smell
- It is a flammable and colourless gas at room temperature
- Its boiling point is -104 ℃ and melting point is -169 ℃
- It is a non – polar molecule and does not dissolve in water

1.1.2 Uses of Ethylene

- Widely used plant growth hormone
- Used as a welding gas
- Used for the production of surfactants
- Used as a raw material for polyethylene, polyvinyl chloride, MEG etc.

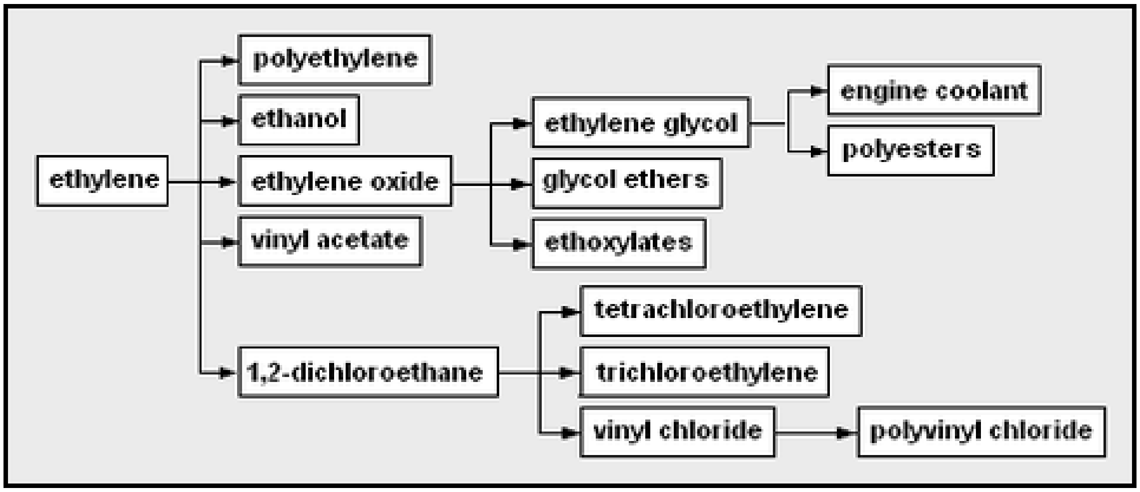


Figure 1.1 Uses of Ethylene (Wikipedia, n.d.)

1.1.3 Commercial Products Being Produced by Ethylene in Pakistan

Ethylene is used as a raw material for three commercial processes in Pakistan. Its scarce use in processes is chiefly due to its price, because it has to be imported at expensive rates from foreign countries.

1.1.3.1 Vinyl Chloride Monomer (PVCs)

Being the world's third most produced plastic polymer, PVC is of paramount importance in this day and age. It is basically synthesized from Vinyl chloride polymer, which is mostly manufactured from Ethylene through Chlorination Method.

The process includes the reaction of Ethylene and Chlorine in a catalytic reactor (with Ferric Chloride being the catalyst) to get an Intermediate known as ethylene dichloride (EDC). EDC is then subjected to thermal cracking at a few hundred degree centigrade, the reaction then follows the free radical mechanism to give Vinyl Chloride Monomer. This method is environment friendly as compared to the previous method where mercuric chloride (which is in substance hazard list) had to be used as catalyst to produce VCM from HCL and Acetylene.

$$C_2H_2 + Cl_2 \longrightarrow C_2H_2Cl_2 \xrightarrow{heat} C_2H_3Cl \ + HCL$$

Ethylene	Chlorine	Ethylene Dichloride	Vinyl Chloride	Hydrogen Chloride

$$C_2H_3Cl \xrightarrow{Polymerization} (C_2H_3Cl)_n$$

Vinyl Chloride Monomer	Polyvinyl Chloride (PVC)

Currently only Engro Polymers and Chemicals limited is producing PVC. Most of the raw material demand is met by importing Ethylene. If there is an extra requirement, Vinyl Chloride monomer (which is itself produced from Ethene as mentioned above) is imported. The capacity of PVC plant is 150000 tonnes per annum. The company had an imported amount of 10000 tonnes in 2009. (dartways, n.d.)

1.1.3.2 Styrene

Pakistan imports styrene in enormous amounts. It is commercially prepared from Ethyl benzene, a derivative of benzene and ethylene, formed by catalytic alkylation in the presence of Aluminium Chloride or a zeolite catalyst.

$$C_6H_6 + C_2H_4 \xrightarrow{AlCL3/Zeolite} C_8H_{10} \Longleftrightarrow C_8H_8 + H_2$$

Benzene Ethylene Ethyl Benzene Styrene Hydrogen

Pak Petrochemicals is the sole producer of Styrene in Pakistan, having an annual production capacity of 90000 tonnes. Due to increased demand, the company is targeting a 40% increase in capacity of the plant at present, and wishes to achieve a 100% rise in the future. Ease in availability of Ethene as a raw material could certainly pave the way for rapid rise in Styrene production. (dartways, n.d.)

1.1.3.3 Polyethylene Terephthalate

Polyethylene Terephthalate is produced by esterification of Terephthalic acid with Ethylene Glycol. Ethylene Glycol is manufactured through the oxidation of Ethylene in the presence of a nickel catalyst, and then reacting the intermediate (Ethylene Oxide) with water.

$$C_2H_4 + 1/2O_2 \xrightarrow{Nickel} C_2H_4O + H_2O \longrightarrow C_2H_6O_2$$

Ethylene Oxygen Ethylene Oxide Water Ethylene Glycol

$$n\,C_2H_6O_2 + n\,C_8H_6O_4 \xrightarrow{220-260°C} (C_{10}H_8O_4)_n$$

Ethylene Glycol Terephthalic Acid Polyethylene Terephthalate

Just like aforementioned products, PET is produced by just one industry in the country. Novatex, with an annual capacity of 235000 tonnes is meeting the ever- increasing demand, especially in the bottling industry. The industry seems to be brimming with success, as it has even started exporting PET. The success graphs would go even higher if Ethylene is easily available. (dartways, n.d.)

1.1.3.4 Potential Products

Pakistan has a very narrow range of plastic products, and imports can't be relied upon for long to meet the sky rocketing demand. The country doesn't have a plant for the production of Polyethylene (the largest produced polymer across the globe). There is high demand for LDPE and HDPE (Low- and high-density polymer Ethylene respectively), so they have to be imported. We were able to approach Mithani Industries Pvt Ltd., and they were of the opinion that availability of LDPE at a lower cost, could help them produce LLDPE (Linear Low-density Polymer Ethylene) bags at a cheaper rate, and even open the doors for new plants by other industrial groups. The demand of another derivative of ethylene ABC (Acrylonitrile Butadiene Styrene) is increasing and Novatex are even looking to produce it here; to meet the requirements of their customers. In such a situation, the chances of a new plant being set up look very bright. In short, Ethylene could prove pivotal in expansion of polymer industrial base of Pakistan.

1.1.4 Import Market of Ethylene and its derivatives

To get an accurate idea of the impact created by Ethylene's trade market on Pakistan's economy, its derivatives must be incorporated in the overall estimation.

The table given below shows the imports of Ethylene and chiefly synthesized chemicals from it from July 2008-April 2009. (Iqbal, 2009)

Table 1 Pakistan's imports from 2008-2009

Name of Chemical	Imports	
	Amount (Kg)	Value (Rs)
Ethylene Dichloride	468,674	46,932
Ethylene	5,405,777	350,256
Styrene	15,778,046	1,619,005
Ethylbenzene	24,714	2,677
Vinyl Chloride	63,350,734	5,134,735
Ethylene Glycol	142,549,884	12,441,756

The second table also shows the annual imports for the same chemicals in the year 2017. (UNdata, n.d.)

Table 2 Pakistan’s imports in 2017

Chemical Name	**Imports ($)**
Ethylene	86,834,361
Styrene	53,480,513
Ethylbenzene	76,565
Vinyl Chloride	8,394,108

Since the database didn’t have the complete information of imports, owing to their purchase at different rates, from a variety of exporters. So, the local rate of 141,658 $/tonnes was assumed, to get a rough idea of the amount imported annually, which came out to be 123000 tonnes.

The following graph shows a summary of the previous imports. (UNdata, n.d.)

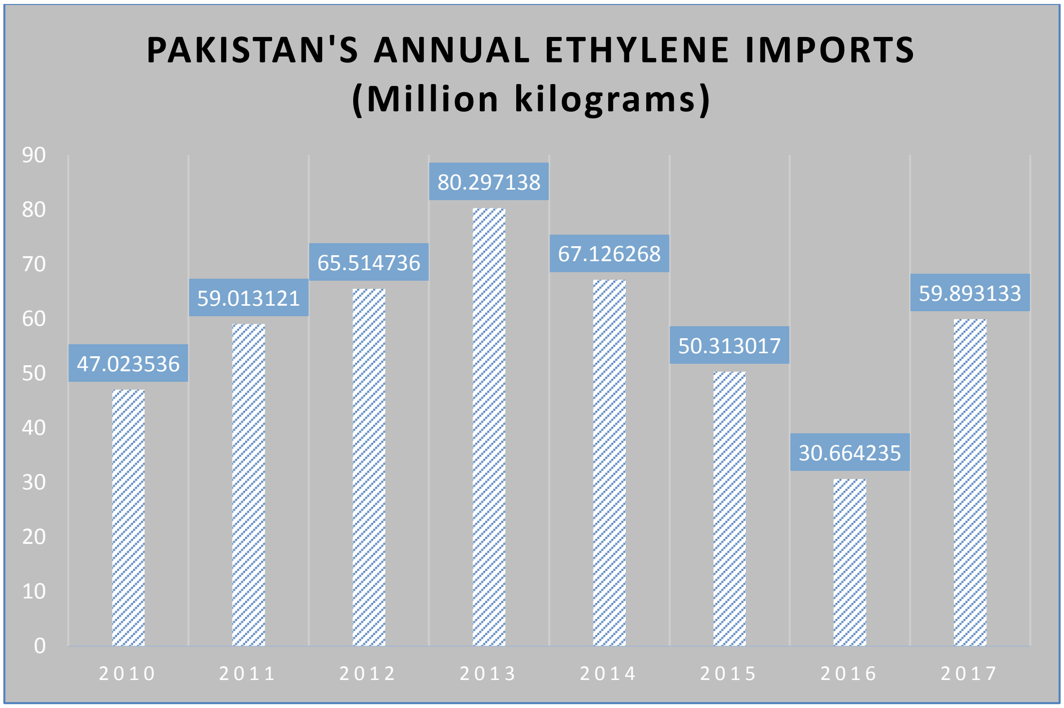


Figure 1.2 Pakistan’s annual Ethylene imports

1.1.5 Contribution of Ethylene in Export Market

Being in high demand, Ethylene is indirectly dominating the global export market with a 25% in share of its polymers. That number balloons up to almost half of the market share, if its impact in the production of other exported plastic products, like Styrene Polymers is taken into account. All in all, having Ethylene can prove to be a key component in climbing up as a Global Plastics Exporter. (SMEDA, 2017)

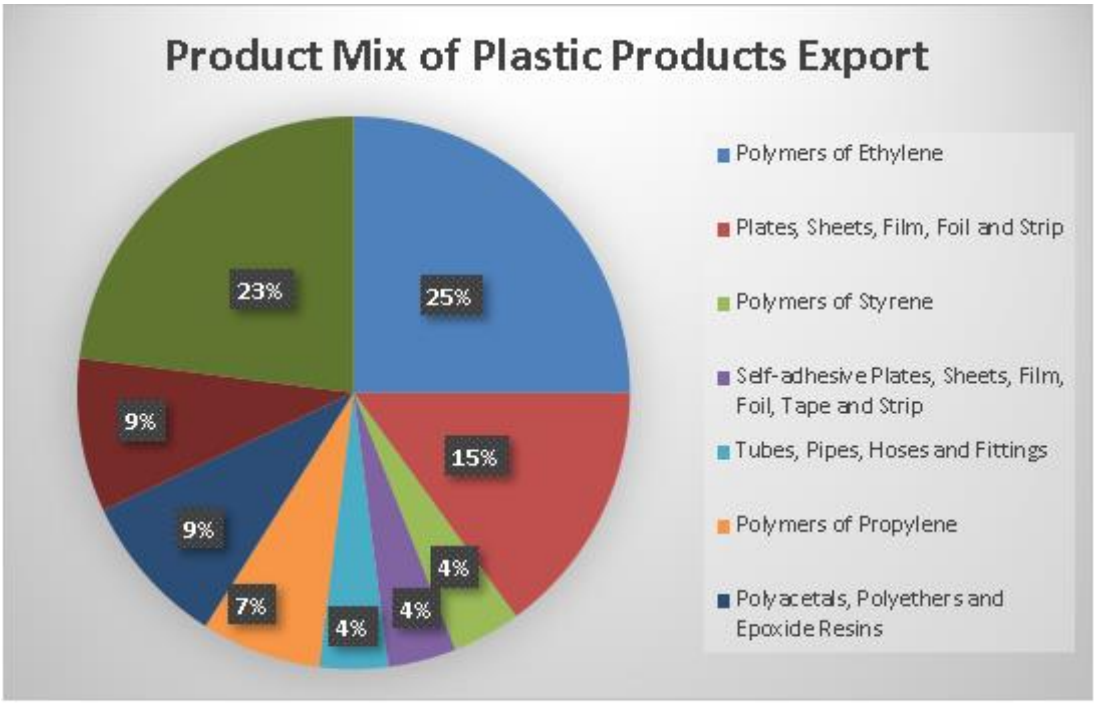


Figure 1.3 Export market of Ethylene products worldwide

The situation of Pakistan is different though, roughly 10-15% of our Plastic imports include Ethylene derived polymers. As suggested earlier, there is a huge market for Ethylene polymers and Pakistan could benefit from it, if Ethylene is cheaper. (SMEDA, 2017)

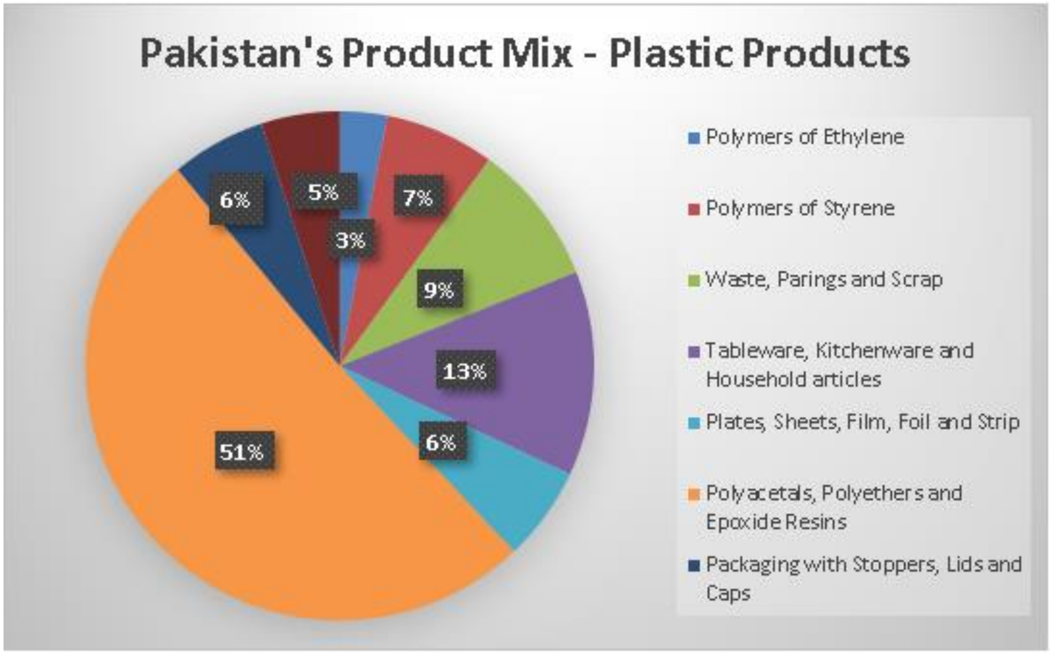


Figure 1.4 Pakistan's import market

The great demand for ethane as indicated by the above stated facts, and a predictive increase in the requirement in the coming years will further emphasize the commercial manufacture of the olefin in the most economical and productive way. The very aim of this project as indicated earlier is to manufacture ethene by ethanol. The following chapter would now be explaining in detail the steps involved in process selection for manufacture of ethene.

2 Process Selection

2.1 Introduction

Many different processes are used worldwide for the production of Ethylene as described below:

- Naphtha Cracking
- Cracking of Ethane – Propane
- Oxidative dehydrogenation of Ethane
- Catalytic dehydration of Ethanol

We will go briefly through each of these processes and then select the one most feasible.

2.2 Naphtha Cracking

After preheating Naphtha, it is mixed with steam and again heated to high temperature. The sudden increase in temperature results in pyrolysis.

The effluent stream is then quenched to terminate further reactions, firstly by indirect quenching with water to 400 – 450°C in transfer line exchanger and then by direct cooling through heavy residue by-products.

Separation of light products of pyrolysis is done in fractionation column. Light products are compressed after that. Then, scrubbing is done by using caustic followed by molecular sieve adsorption to remove Sulphur compounds, Mercaptan, etc.

The products are then sent to the cold section which comprises of demethaniser, deethaniser, depropaniser and Ethylene separation steps. In the end, Ethylene, Propylene and similar products are obtained. (NPTEL, n.d.)

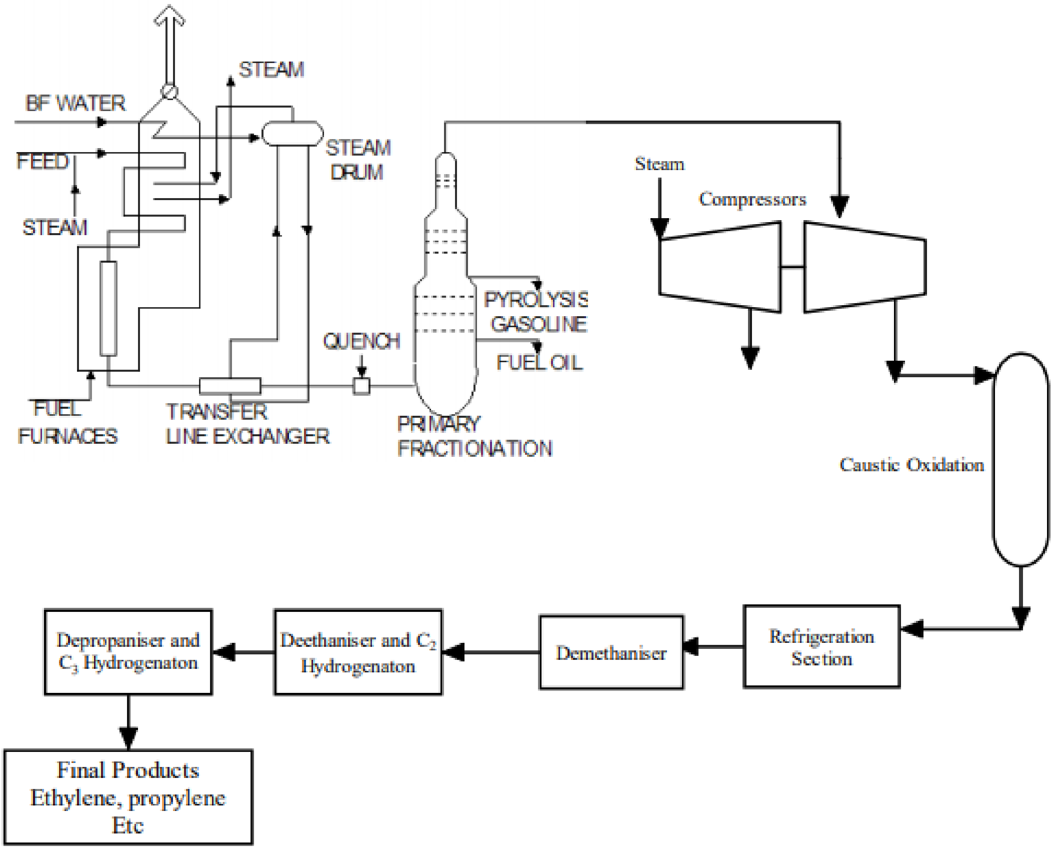


Figure 2.1 Descriptive diagram of Naphtha Cracking

2.2.1 Advantages of Naphtha Cracking

- Cuts out the expensive distillation processes
- Large variety of products
- Low carbon deposition

2.2.2 Disadvantages of Naphtha Cracking

- Energy intensive process
- Environmental hazards
- Finite resources in Pakistan
- Low yield of Ethylene
- Less purity compounds produced

2.3 Cracking of Ethane - Propane

In this process, an Ethane-Propane mixture is first cracked producing Ethylene, Propylene and other by-products. This stream is quenched, to prevent any more reactions and formation of undesired products. Cracked gas is then directed to compression. After compression, caustic scrubbing is done to eliminate Carbon dioxide and Sulphur. The gas is then cooled and dried by molecular sieves to eliminate water.

Compression is followed by drying of the cracked gas, it is entered into a cold box for the elimination of hydrogen and light hydrocarbons, while decreasing ethylene losses to a minimum. The products from chilling train are entered into a series of separation columns of demethaniser, deethaniser and depropaniser. Polymer grade Ethylene is removed from the deethaniser as a side stream. (Chemical Engineering, n.d.)

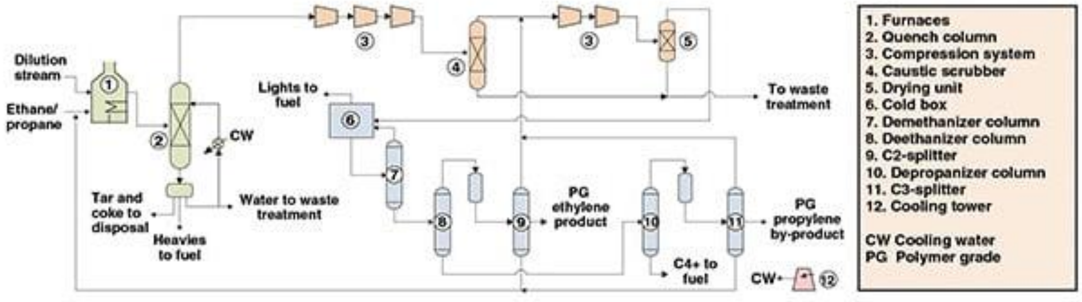


Figure 2.2 Cracking of Ethane-Propane

2.3.1 Advantages of Cracking of Ethane – Propane

- High variety of products is formed
- Low carbon deposition

2.3.2 Disadvantages of Cracking of Ethane – Propane

- Energy intensive process
- Low yield of Ethylene
- Less purity achieved

2.4 Oxidative dehydrogenation of Ethane

In this process, Ethane is used as a feedstock. Firstly, it is heated at a high temperature through a network of heat exchangers. The heated Ethane is then sent to a catalytic reactor where it is dehydrogenated in the presence of oxygen. The effluent is sent to a cooling network where it is cooled down and separated from water. It is then passed through membrane network from where Ethane is recycled and Ethylene is sent forward. (Anne M. Gaffney, 2017)

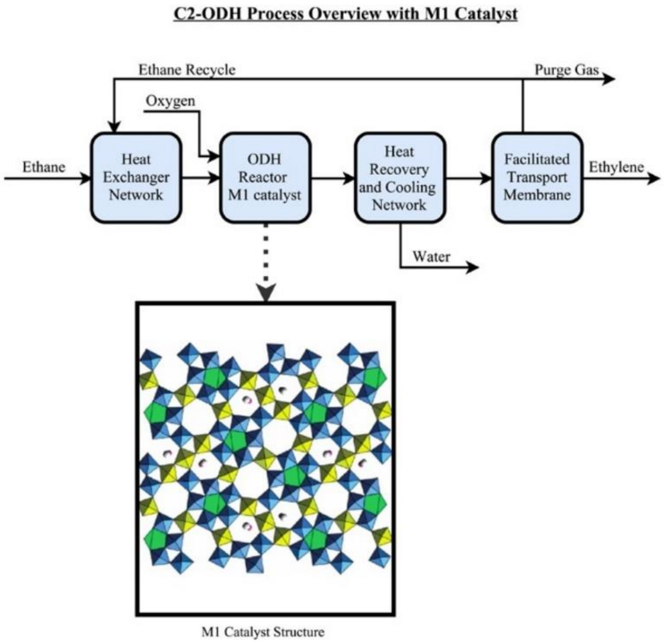


Figure 2.3 Oxidative dehydrogenation of Ethane

2.4.1 Advantages of oxidative dehydrogenation of Ethane

- High selectivity of Ethylene

2.4.2 Disadvantages of oxidative dehydrogenation of Ethane

- High energy requirements
- Coke formation
- High endothermicity

2.5 Catalytic dehydration of Ethanol

Ethanol is sent to the reactor after preheating it. In the reactor, after interaction with the catalyst, Ethanol dehydrates and produces mainly Ethylene (at temperature above 573K) while Diethyl ether is also produced if the temperature goes below 573K. Other by-products like acetaldehyde, hydrocarbons etc. may also be produced in very low amounts. After the reactor, the products go to the washing towers, dryer and light-end, heavy-end towers for the separation of other by-products. The following diagram shows the process flow:

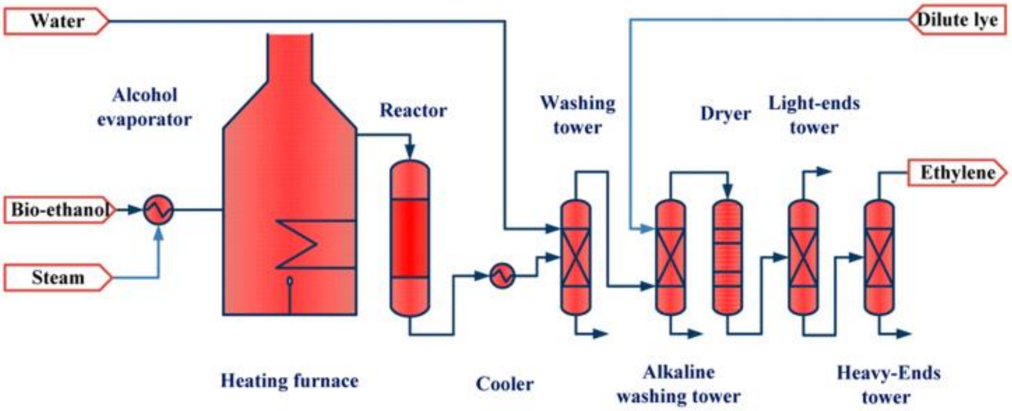


Figure 2.4 Catalytic dehydration of Ethanol

The process operates at around 300-500 ℃, 0.1 – 0.2 MPa and 0.1- 1 hr^{-1} space velocity. 94-99% of Ethylene can be achieved by this process depending on the catalyst chosen. (Minhua Zhang, 2013)

2.5.1 Advantages of catalytic dehydration of Ethanol

- Abundant Ethanol in Pakistan
- Low temperature conditions
- Regeneration of catalyst possible
- High selectivity of Ethylene

2.5.2 Disadvantages of catalytic dehydration of Ethanol

- Expensive catalyst

2.6 Why catalytic dehydration of Ethanol?

There are a number of reasons as to why this pathway is being selected for the production of Ethylene:

1. Pakistan is self-sufficient in the raw material – Ethanol. We have a large number of sugar mills producing sufficient quantities of Ethanol to export. Those can be easily utilized here for the production of Ethylene – one of the main chemical backbones of any country, to minimize its imports. As for the other raw materials for above described processes:
    - Naphtha is also produced in large quantities in Pakistan. As of 2015, Naphtha exports were 1074,000 metric tons. That is why, some work has

already been done for the establishment of Ethylene plant by naphtha cracking.

- Ethane, Propane etc. are also present in Pakistan in the Sui reserves in large quantities but these are non-renewable resources and are rapidly depleting day by day. So, the usage of such depleting resources for the production of other chemicals seems illogical when other raw materials are present in huge amounts.

2. All the other processes produce a range of by-products which reduces the amount of target product- Ethylene. Also, a long separation train is required for these by-products. This increases the cost and energy requirements for overall plant.
   The selected process has a very fewer by-products which can further be minimized by the use of catalyst HZSM-5. So, a smaller separation assembly is required.
3. All the other processes require very high temperatures which in turn means that they have higher energy consumptions.

2.7 Production of the Raw Material (Ethanol) in Pakistan

The production of Ethylene requires ethanol as the raw material. Ethanol is produced in large quantities all around Pakistan by the treatment of sugar molasses. Sugar industry is the 2nd largest industry in Pakistan after textile. Ethanol is the end product of a three-stage process including:

1) Sugar cane production
2) Sugar refining
3) Conversion of molasses into Ethanol (PEMA- Pakistan Ethanol Manufacturers Association, n.d.)

   There are 3 main types of Ethanol:

1) Fuel (Crude grade, fuel blending, 80% of the world's production)
2) Industrial
3) ENA (Extra Neutral Alcohol) (Hussain, 2015)

According to the data of 2012, there were 84 sugar mills in the country, with a crushing capacity of 465,000 tons of cane per day. (Tariq Ali, 2012) But not all the sugar mills have a capacity to produce ethanol after the fermentation process of molasses. The production ratio of molasses to Ethanol is 5:1. (Rehman, 2008)

Only the annual production of one industry, UNICOL, is 55000 metric tonnes. It produces premium Extra Neutral Alcohol (ENA):

ENA anhydrous 99.9%

ENA > 96%

B Grade > 92% (Head & Tail) (Unicol, n.d.)

Pakistan Ethanol Manufacturers Association comprises of 20 Ethanol distilleries under it.

In 2015, Pakistan's annual total capacity of Ethanol production was 750,000 MT which made Pakistan the 4th largest exporter of Ethanol in the world (if all grades are considered). If only ENA and Industrial grades are considered, then Pakistan is the 3rd largest exporter of ethanol around the world. Pakistan's Ethanol is used in around 60 countries.

In 2016 Pakistan fuel Ethanol production was at level of 0.2 thousand barrels per day. Fuel Ethanol is the ethanol which is made anhydrous (less than 1% water) and is intended for fuel use. (Knoema, n.d.)

In 2017, the overall volume exported in April was 42,100 tonnes, against 77,000 in March and 60,000 in April.

In 2018, cumulative exports so far have reached 180,000 tonnes against 161,000 tonnes in the same period a year ago. (RVBCompany)

The following graph shows a summary of past Ethanol exports by Pakistan: (UNdata, n.d.)

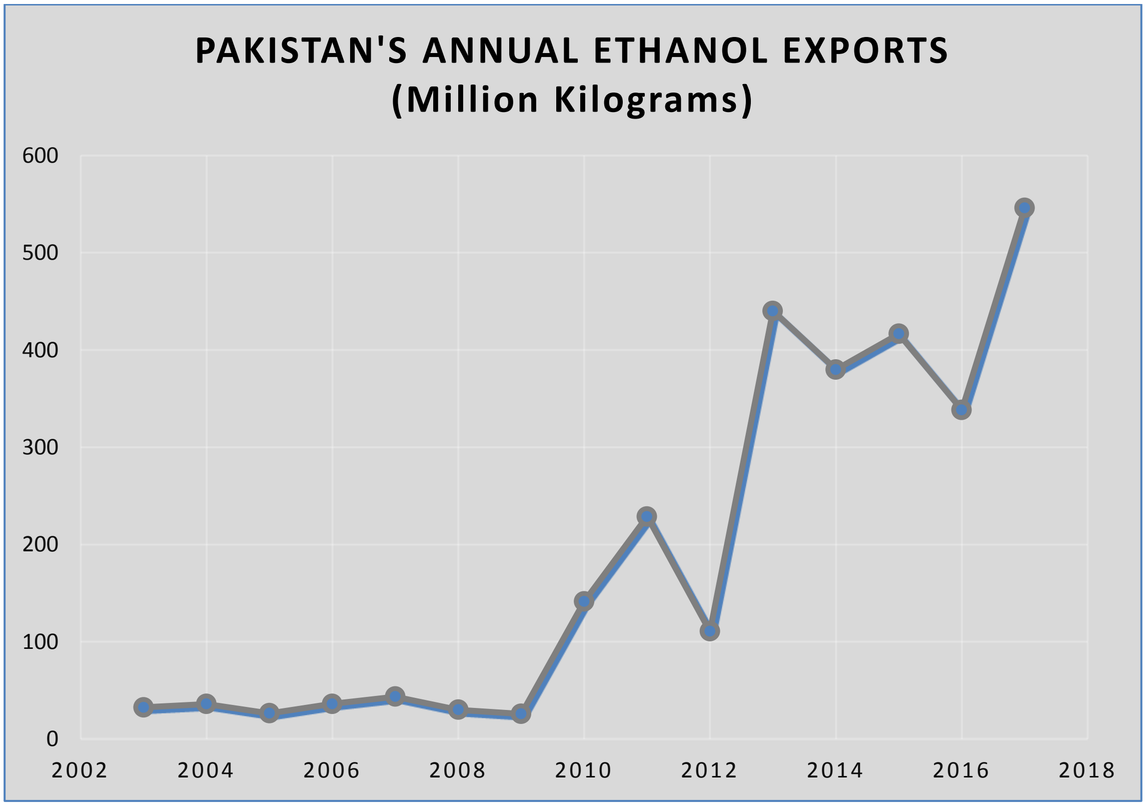


Figure 2.5 Summary of Pakistan's Ethanol exports

3 Process Description

The manufacture of ethanol into ethene is basically carried out in two major steps. The first one is the conversion of ethanol to ethylene over a catalyst along with formation of water and some other by-products.

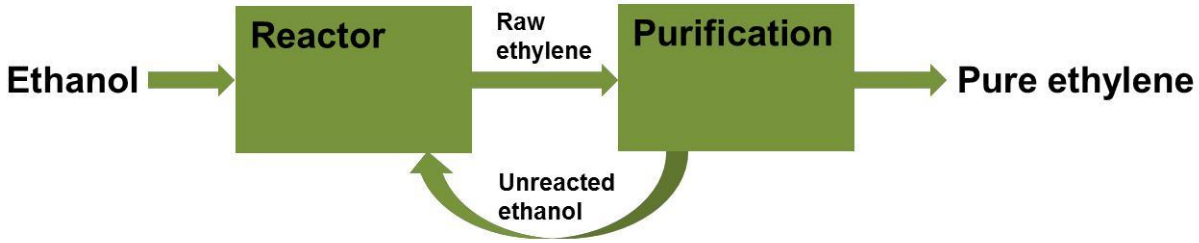


Figure 3.1 Steps of Ethylene Synthesis from Ethanol

The second step is the purification of the products to obtain ethylene of polymer grade purity. A gas liquid separator is first employed to remove liquids including water and ethanol. In most cases ethanol is recycled to the reactor (if the amount is appreciable). An absorber is installed to capture Carbon Dioxide and for absolute removal of water become going into cryogenic conditions an adsorber is used. In cryogenic distillation, ethylene is first purified from heavier hydrocarbons in ethylene column, subsequently followed by a C2 stripper where ethylene emerges as the bottom product, separated from CO and H_2.

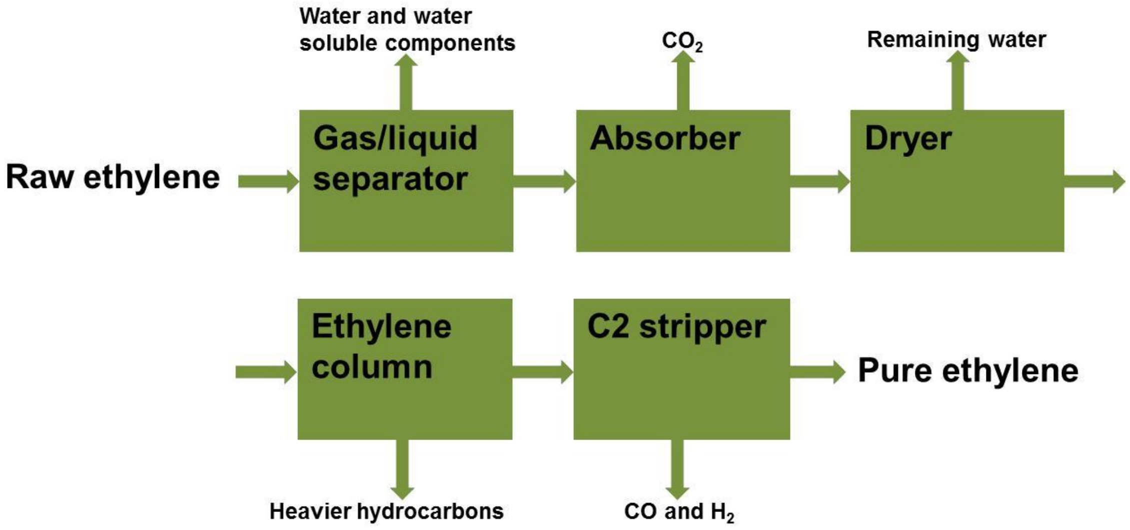


Figure 3.2 Purification steps for Ethylene synthesis

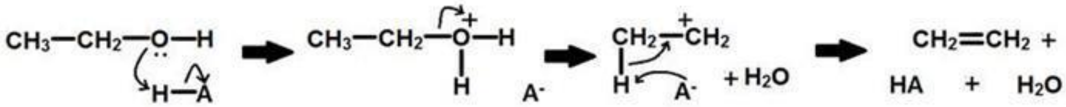


Figure 3.3 Mechanism for Conversion of Ethanol to Ethene

3.1 Dehydration of Ethanol to Ethene over a Nano-zeolite Catalyst

Dehydration of ethanol to ethene is a relatively environment friendly alternative for getting the olefin. The reaction is basically carried out in the vapor phase at temperatures ranging from 180-500 ℃ inside a fluidized or a fixed bed reactor. (Mohsenzadeh, 2017)

The approaches of proceeding with the reaction generally employed are though Isothermal or Adiabatic reactions.

3.1.1 Fixed Bed Reactor

Fixed bed reactor technology has been the most widely used one for this process. The very reason for that is their wide-scale and proven commercial application. Although they provide good conversion, they cannot be utilized in reactions where hot spot formation is a concern.

3.1.1.1 Isothermal Approach

In Isothermal fixed bed reactor, a multi tubular arrangement is implemented with the catalyst packed in the tubes, while the reactant (ethanol) flows over it. To imagine the working of a tubular reactor, it may as well be assumed as a shell and tube heat exchanger, with the hot fluid (steam) flowing through the shell side and vaporized feed flowing the tubes over the catalyst. The need of heating through steam arises because of the fact that the temperature of the reaction falls owing to it being endothermic, and maintenance of temperature is pivotal to the yield as well as selectivity of the process. The advantage with the isothermal approach is the high conversion that it provides, for such reactions. The fact that fixed bed reactors are prone to hot spot formation also makes the isothermal approach the better one, with it being able to give very decent uniformity in terms of temperature.

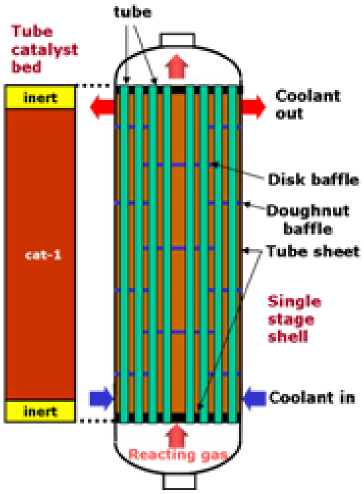


Figure 3.4 Fixed tubular reactor

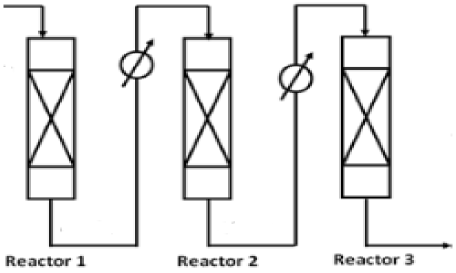


Figure 3.5 Reactor series

3.1.1.2 Adiabatic Approach

A series of packed bed reactors are utilized in this process, with heating provides in between. The conversion is pretty low since the reactors are adiabatic and the temperature falls due to the endothermic nature of the reaction, and that is why they are employed in the series to achieve the desired conversion. (Mohsenzadeh, 2017)

3.1.2 Fluidized Bed Reactor

Decent conversion with extremely high selectivity can be achieved with in Fluidized bed reactors. No external heat is required to maintain the temperature, since the heat generated by continuous regeneration of the catalyst is utilized. These reactors provide great heat and mass transfer and the formation of temperature zones is very rare or almost non-existent. The problem though is that they haven't been tested enough on the commercial scale, according to our research. Till now, barring an exception or two fluidized bed reactors have been restricted to laboratory scale. (Mohsenzadeh, 2017)

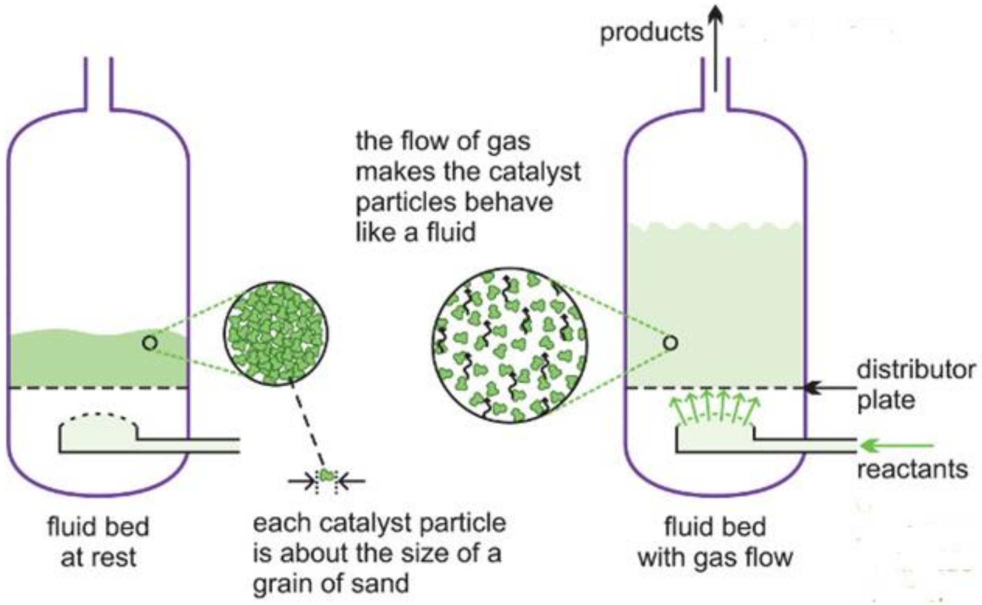


Figure 3.6 Fluidized bed reactor (The Essential Chemical Industry - Online, n.d.)

3.1.3 Catalysts for dehydration of Ethanol

Catalyst selection can do a world of good to the efficiency of a process and specially in case of ethanol dehydration. We could be working with extremely high temperatures with one catalyst while some other catalyst could be offering a drop of 200-300 K to the required temperature. Same goes for the equipment and the tendency of by-products to form. The parameters can change drastically with the slightest of changes in the catalyst decided.

It has already been mentioned above that ethanol dehydration is basically and acid catalysed reaction. Heterogenous catalysts are generally used to catalyse the process. They can be classified into 3-4 major kinds, which have been discussed below but a rather – emphasis has been made on the class of catalyst that was finalized. (Yakovleva)

3.1.3.1 Phosphoric Acid Catalysts

The use of Phosphoric acid catalyst for the process goes back to 1930's when they were first synthesized by loading phosphorus on Coke or clay. Their use however was shunned in the midst of the 20th century, particularly due to regeneration problems. They offered a somewhat decent purity, but it came at a greater cost. The catalyst had to be regenerated very often because it was easily deactivated by coke, and the very fact that its regeneration took a month didn't bode well.

3.1.3.2 Metal Oxide Catalyst

Metal oxide catalysts with acidic properties are highly used on Commercial scale. In this process though, Alumina is predominantly used, and very rarely another metal oxide is opted for. Even while judging over a broader spectrum Alumina is by far the most utilized catalyst for ethanol dehydration. Almost all plants established in the 20th century are running over Alumina, and in this century as well, the stakeholders have been reluctant to switch to another alternative.

In the early phase when it replaced Phosphoric Acid systems Alumina was offering slightly lower conversion of about 96-97% with considerably lower coking tendency.

Later Lumnus used gamma Alumina in a plant in India with a conversion of almost 99%. It was then followed by Syndol (a multi-oxide catalyst) which increased the ethylene selectivity and conversion of ethanol to 97% and 96-99% respectively.

Many other modifications have been made, but gamma Alumina has been widely used specially in the 20th century. It's basically a porous crystalline form of Al_2O_3, with a surface area of around 180 m^2/g. Apart from the technology used by Lumnus, its conversion has been hovering around 80% percent.

Whilst the conversion seems adjustable by doping and modifications like the ones mentioned above, extremely high reaction temperature of around 300-450 ℃ poses an even greater problem. The higher temperature doesn't just increase the cost, it damages the catalyst as well and the activity drops considerably with time. Even regeneration is not feasible in some cases. Water is also produced in the reaction and it also damages the active sites of Alumina thus reducing the conversion to ethylene.

3.1.3.3 Molecular Sieve Catalysts

Materials like molecular sieves which have a porous structure provide a large surface area and offer unique basic and acid properties. They can be used as catalysts, adsorbents or ion-exchange materials depending upon the type of operation.

They have been in great use since 1980, the majorly used types have been ZSM-5 (Zeolites), SAPO (Si-Al phosphates), AM-11 and A. SAPO serves better for use in methanol dehydration. Zeolites are the most suitable class for this reaction. Zeolites are basically Alumina Silicates in crystalline form with microporous structure and a surface area of about $900m^2$/g. Their structure makes them very flexible for a vast variety of processes. Their pores have cations which can either be exchanged or their size can be varied to alter the catalyst depending upon the situation.

Initially research was carried out on ZSM-5 and the fact that reaction had to be carried out at very high temperature of around 573K-673K made it an extremely unstable. It was then modified into HZSM-5 through ion-exchange. HZSM-5 is highly useful as it gives an ethanol conversion of around 98% and ethylene selectivity of about 95% at a low temperature of 473K. It’s higher acidity though promotes coking and causes it to deactivate rapidly.

Several techniques have been employed to decrease Zeolite acidic behaviour, so as to enhance stability. The two modifications that stand out as the most feasible ones are that of Lanthanum Phosphorus and Nano-cat. Nano-cat was basically formed by mixing powdered form of 70 percent by weight Nano-HZSM with 30%w Aluminium Oxide (in powdered form too). (Yaochi Hu) (Bi, 2009)

3.1.3.4 Selection of the Catalyst

As mentioned above, the selection of catalyst was an important aspect in finalizing the process. Catalyst were evaluated on the basis of the following parameters.

- Coking Resistance.
- Reaction Temperature.
- Regeneration Mechanism.
- Ethanol conversion and Ethylene selectivity.

Of all the aforementioned catalysts Alumina and stable forms of Zeolites are the most viable and widely used option. Phosphoric acid systems haven't been used since 1950's and Heteropoly acids are at a very nascent stage at the moment so their commercial use is limited.

The problem with Alumina is that the reaction temperatures are really high, conversion and selectivity are relatively low, and the coking tendency is extremely high (500-700 K). Regeneration though is possible in some cases, while there are some instances where extremely high temperatures damage the catalyst and it's not economically feasible to regenerate it.

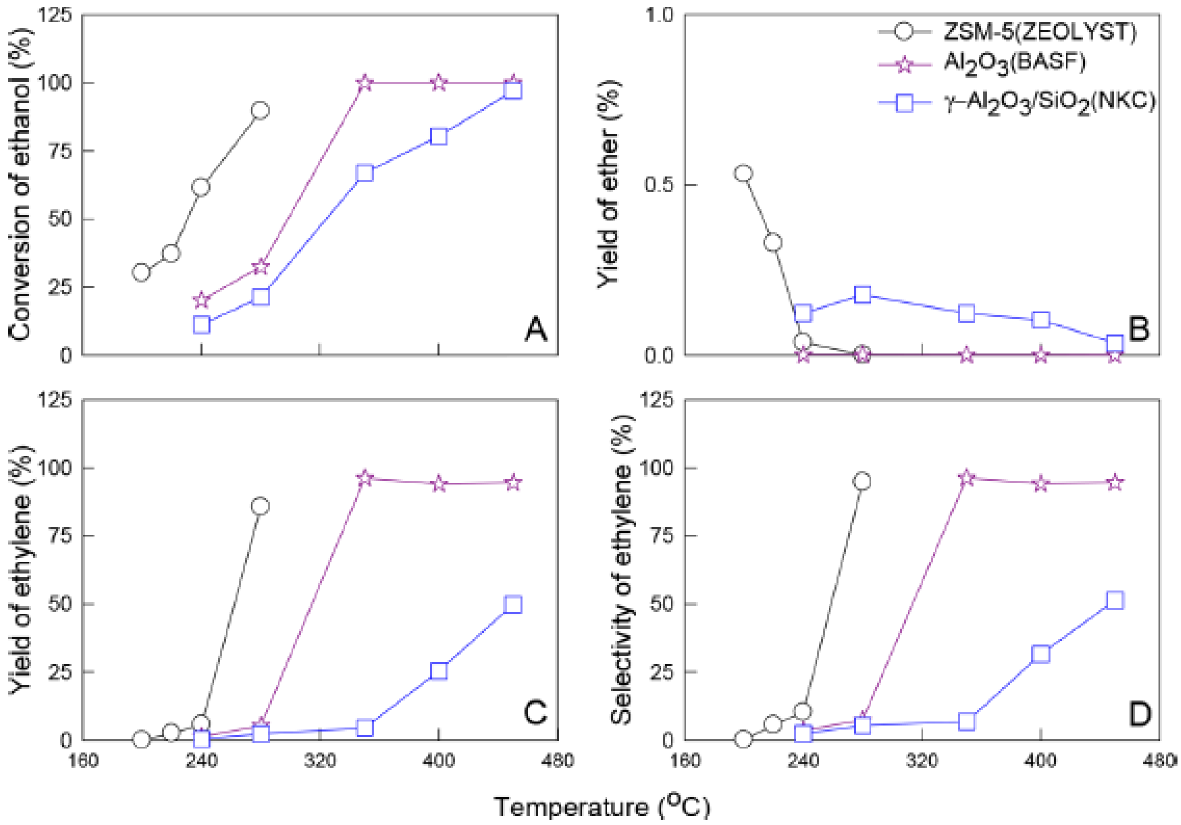


Figure 3.7 Comparison of performance of catalysts vs Temperature (Wu, 2017)

Zeolites carry out the reaction at a low temperature with high conversion and selectivity, but their coking tendency is higher, the reason being high acidic site.

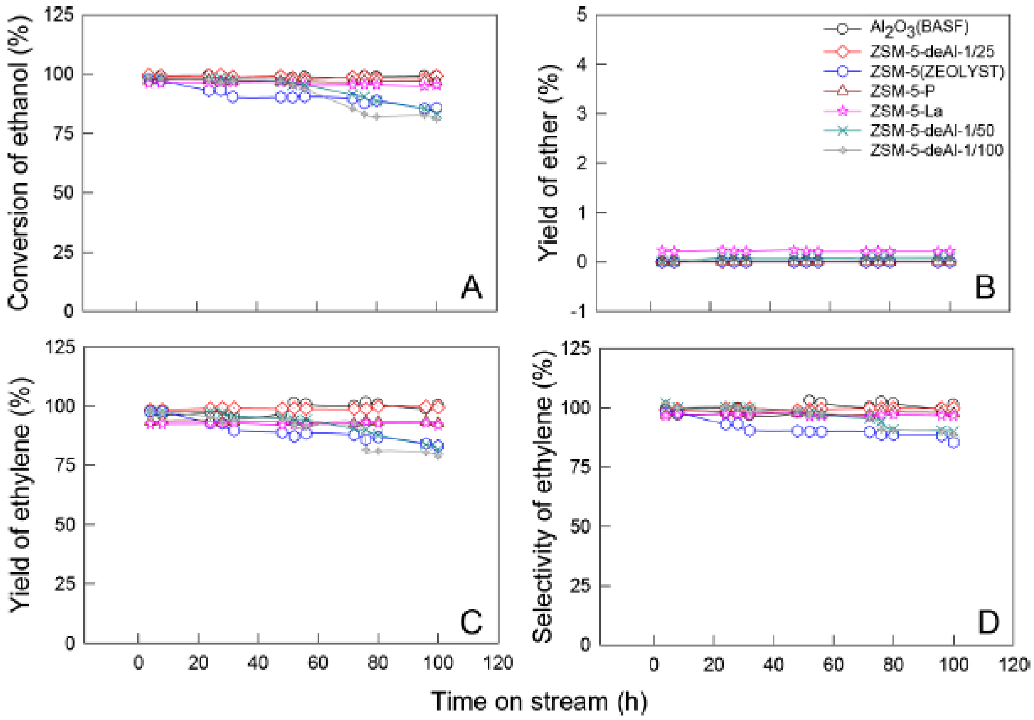


Figure 3.8 Comparison of performance of catalysts vs Time on stream (Wu, 2017)

Heteropoly acids are somewhat similar to zeolites, the reaction with them as catalysts takes place at around 160-170℃. Their conversion though, is very low, and multiple reactors have to be connected in series to get the desired amounts. The costs can go high as the reaction is endothermic and heating is required between reactions.

After going through all the possible catalysts, Nano-Cat and Lanthanum Phosphorus were shortlisted. Both these options were equally good, but the lifespan of the latter type was somewhat dubious, so Nano-cat was decided as the major catalyst. The following section covers Nano – HZSM 5 and how it is the best alternative to the conventionally used catalysts.

3.1.4 Nano-CAT

Nano-CAT is prepared by extrusion of a mixture of 70 percent powdered form of Nano-scale HZSM with 30 percent by weight Al_2O_3 powder, while using 0.5 mol/litre Nitric Acid solution as an adhesive, followed by drying and calcination for 15 and 4 hours (at 540 ℃) respectively. (Bi, 2009)

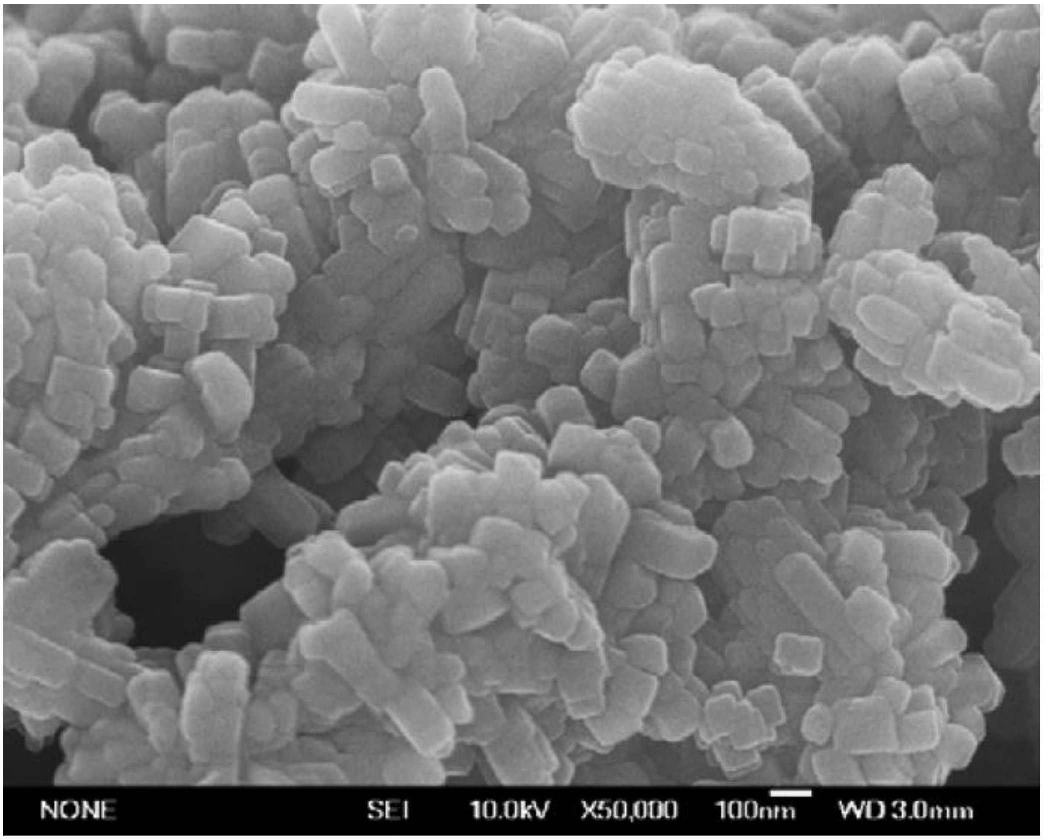


Figure 3.9 SEM for Nano CAT (Bi, 2009)

Nano-CAT provides higher selectivity and conversion of ethylene and ethanol at a low temperature while at the same time being extremely stable to coking. (Bi, 2009)

- Nano – CAT due to its smaller crystal size as compared to Micro – CAT provides a shorter diffusion path to ethylene which basically inhibits the contact time of the olefin with the strong Bronsted acidic sites capable of increasing polymerization and thus producing carbonaceous deposits.
- Another thing that makes the Nano-form better is its lower ratio of acidic sites inside the pore to the actual number of active sites. This combined with the shorter diffusion path makes the deactivation time of Nano-CAT longer, thus giving it a good life span of 630 hours (before its selectivity lowers to 98%).

Table 3 Comparison of Nano- and Micro- HZSM 5 (Bi, 2009)

	Nano-HZSM 5		**Micro-HZSM 5**	
Ethanol Concentration	45	95	45	95
N_2 Carrier Gas	0	2.1	0	2.1 l/sec
Weight Hourly Space Velocity (1 h-1)	0.8	1	0.8	1
Stream Time	260	420	50	100
Gaseous Phase (mole percent)				
C_2H_4	97.57	98.67	95.98	98.02
$(C_2H_5)_2O$	0.50	0.04	2.04	0.05
C_2H_6	0.07	0.04	0.14	0.08
C_2H_4	Traces	Traces	Traces	Traces
C_2H_5O	0.46	0.56	0.53	1.08
C_3	0.54	0.23	0.52	0.15
C_4	0.50	0.27	0.59	0.26
C_5	0.07	0.05	0.19	0.06
$>C_6$	0.12	0.06	0.19	0.07
CH_4	Traces	Traces	Traces	Traces
H_2O	99.67	99.74	98.34	99.63
Liquid Phase (mole percent)				
C_2H_5OH	0.31	0.21	1.60	0.36
C_2H_4	Traces	0.05	Traces	Traces
$(C_2H_5)_2O$	Traces	Traces	0.05	Traces
C_2H_4 Selectivity	96.48%	98.69%	93.00%	98.71%
C_2H_5OH Conversion	98.27%	99.20%	92.92%	97.79%

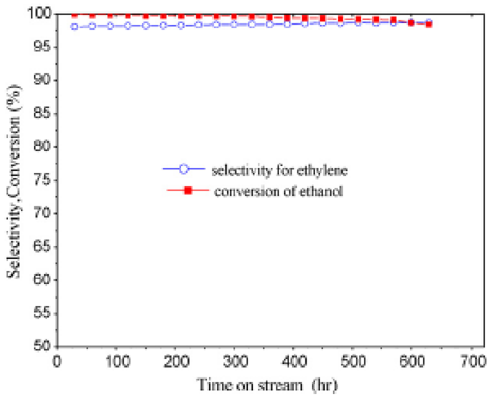


Figure 3.10 Nano HZSM-5 (Bi, 2009)

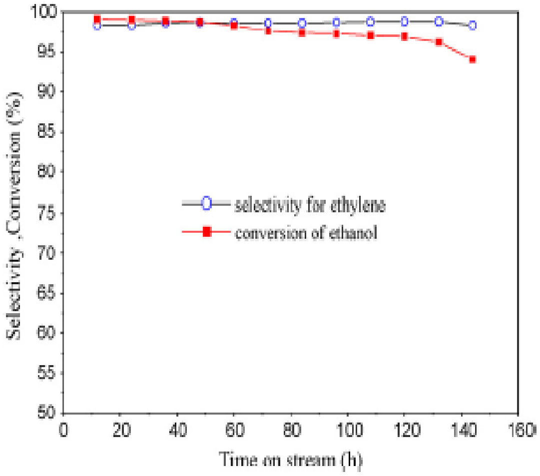


Figure 3.11 Micro HZSM-5 (Bi, 2009)

Table 4 Comparison of Nano- and Micro- HZSM 5 acidic sites (Bi, 2009)

Catalyst	**External surface Acid sites (mol/g)**		**Total Acid sites**		**External/total %**	
	$H_o \leq +2.27$	$H_o \leq +4.8$	$H_o \leq +2.27$	$H_o \leq +4.8$	$H_o \leq +2.27$	$H_o \leq +4.8$
Micro-Cat	100	100	100	1300	10	8
Nano-Cat	50	300	100	800	50	37.5

3.1.4.1 Coking

For heterogeneous acid catalysed reactions coking is extremely detrimental and curbing it extremely difficult. Oligomerization and polymerization are the two major causes of coking, as shown in the reaction below.

$$C_xH_y \longrightarrow polymerization \longrightarrow Coke + nH_2$$

Oligomerization is favoured by higher carbon to hydrogen ratio (x/y) in the hydrocarbons, and so owing to a greater number of double bonds, there is a tendency to oligomerise. Ethylene itself is major cause for low conversion in ethanol dehydration because of its highly reactive nature which subsequently aids coking.

Coking can be handled in the following ways

- By lowing the residence time of ethene, smaller the time interval ethylene molecules are in contact with the catalyst, smaller would be the coking tendency in return.
- By lowering the acidity of the catalyst coking can be managed for these reactions, because strong acidity (particularly in case of zeolites) is a chief contributor in the coking phenomenon.
- By adding water or other similar suppressants coking can be reduced to a degree

3.2 Commercial Technologies for Ethene Manufacture from Ethanol

3.2.1 Process Description

Ethanol feed containing water in small amounts stored in a vessel at STP, is first pumped to a pressure of 1.5 bar to be preheated to 85℃. After that superheated steam is utilized to superheat the feed to the required reaction temperature of 240℃, before being fed to an Isothermal packed bed reactor.

The reactor is kept Isothermal by steam exiting the second exchangers (i.e. the super heater). Ethanol is converted to ethene and water, along with the formation of by-products. The product stream is then split into two streams, before being cooled. 70% of the product is used to preheat the feed, while the rest is cooled through use of cooling water.

The two streams are mixed again after exiting the preheater and first cooler respectively, before being cooled to a temperature of 30℃. The outlet stream is then fed into the first gas liquid separator, where bulk of liquids are separated on the basis of density difference. The liquids exit from the bottom while the gases emerge from the top.

The top of product the first separator enters the second gas liquid separator called Gasunie separator, where swirling produces almost 100% removal of liquid. Gasunie separator top stream is then passed through a 3-stage compression train with inter-stage cooling to get the pressure from 1 bar to 22 bar for Cryogenic Separation.

The compressed stream is first cooled through water to before ethylene refrigerant at -70℃ is used to reach the cryogenic temperature of -28℃. In cryogenic distillation ethylene having a lower boiling point comes in the distillate with 99.9% purity.

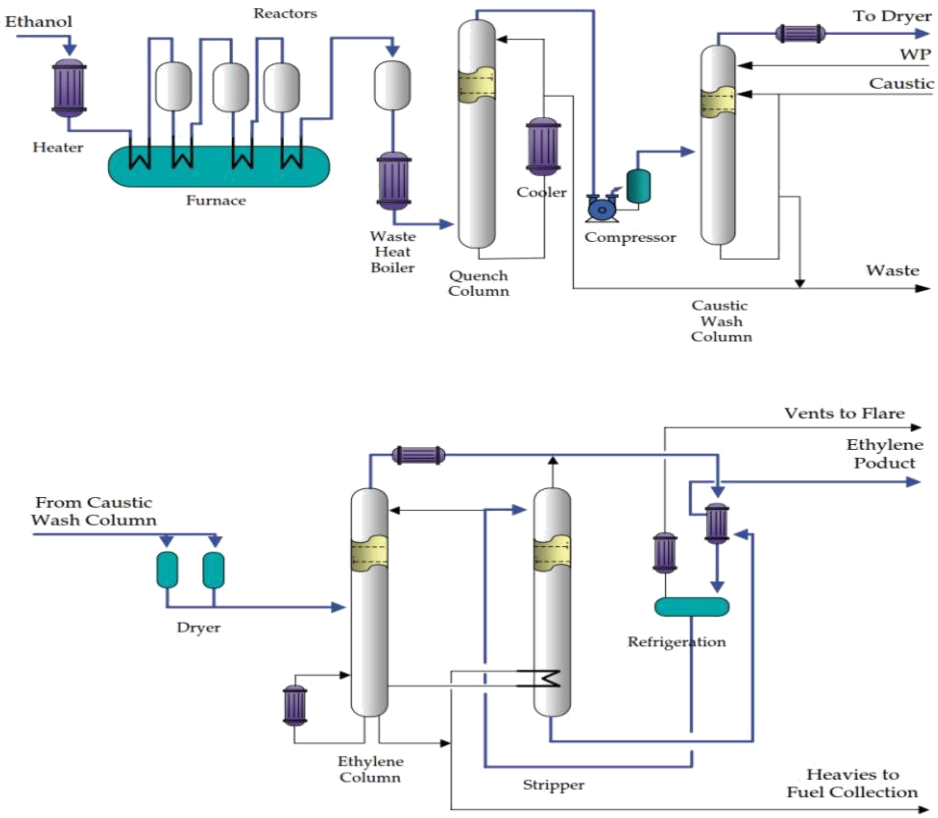


Figure 3.12 Commercial process of Ethene from Ethanol

3.2.2 Detailed description of our process

The detailed description of our process along with the process flow diagram is as given below.

(1) **Multi-Tubular Fixed Bed Reactor:** As mentioned earlier, catalyst is packed in the tubes in a multi-tubular reactor, while the cooling or heating media flows in the shell. In this process the tubes are packed with Nano-CAT with ethylene flowing over it, and steam from the outlet of super heater flows in the shell to maintain isothermal conditions. The conversion of ethanol achieved is 99.2 % with ethylene selectivity being 98.69 %.

(2) **Vertical Knock Out Drum:** The first separator is basically a vertical gas liquid separator without a demister pad. The purpose of this separator is to relieve the liquid load of the cyclone separator, and the separation is carried out on the basis of density different with gravity being the driving force upon provision of the required holdup time. Feed entering it is atomized by a nozzle which aids in gravity playing its part. (Griffith, n.d.)

(3) **Gasunie Cyclone Separator:** To protect the impellers of the compressors from damage, and the plates of distillation column from freezing it is immensely important to remove all of the water or any liquids that might be present. For that purpose, a highly efficient form of flash separators, Gasunie cyclone separator is employed. In this kind, the feed is subjected to swirling motion with the liquid moving away towards the walls through the vanes, while the gas easily flowing down through the vortex cone and be collected at the bottom. With implementation of an inverted cone called a Chinese hat, it is ensured that no liquid enters the vortex cone. Unlike the former type, the pressure drop in Gasunie separators is generally high. (International, 2007)

(4) **Distillation Column:** Cryogenic distillation is the costliest and an extremely important step in the ethylene manufacture be it from naphtha cracking or ethanol dehydration. In the distillation column sieve trays are employed, the light key (ethylene) flows through the sieves, since it is vapor while the heavier liquids flow down through the downcomer after having gone through mass transfer in a phenomenon described as froth formation. (Perry)

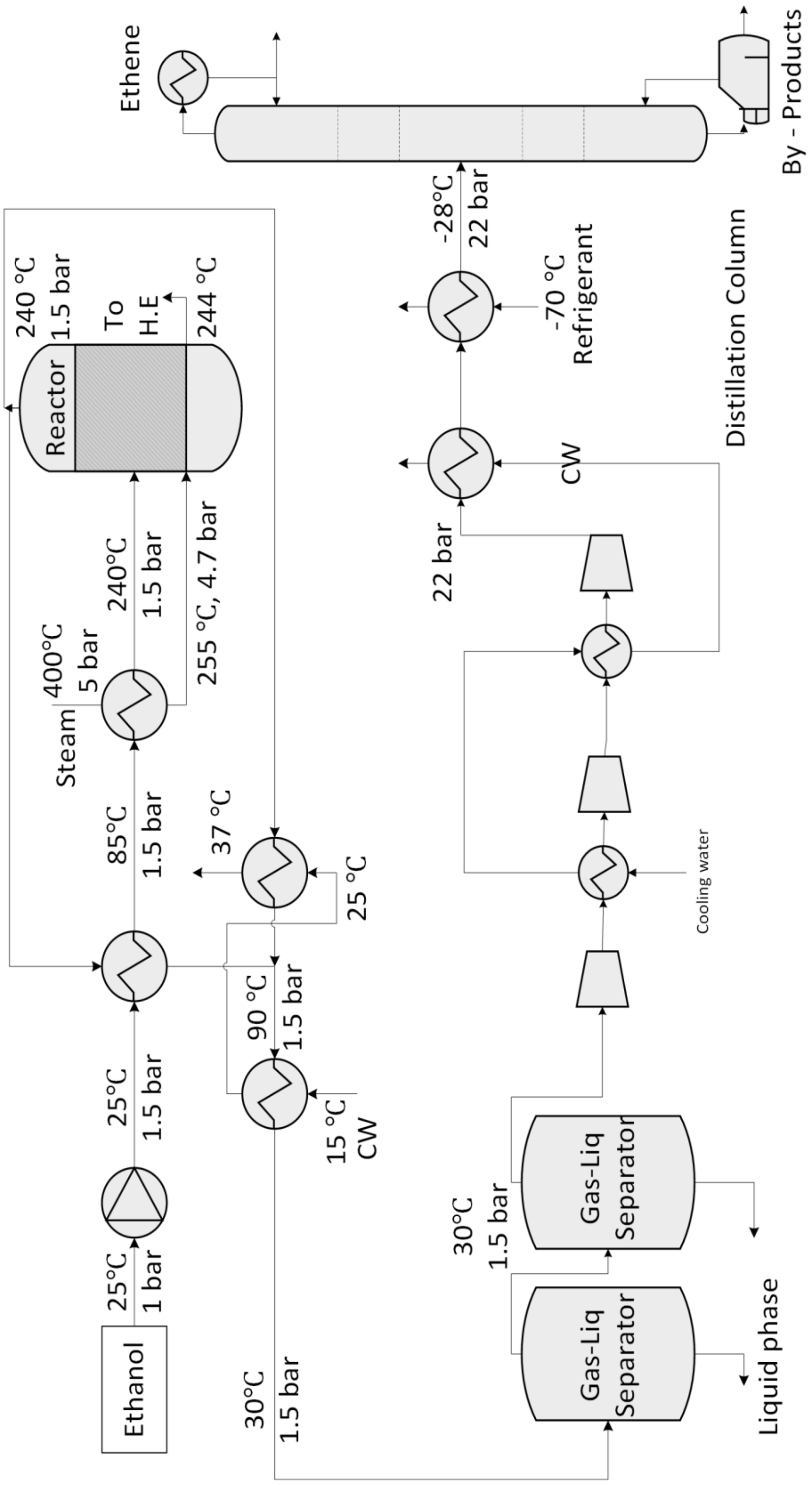


Figure 3.13 Our Process Flow Diagram

4 Material Balance

4.1 Feed composition

The raw material feed is 95% v/v Ethanol with water. According to the imports data, required capacity of plant has been taken to be 60 tons/day of Ethylene.

60 tons/ day = 89.3 kmol/hr ≅ 90 kmols/hr of Ethylene

According to the balanced chemical equation,

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$

For 90 kmol of Ethylene, we require 90 kmol of Ethanol.

Since the feed is not all Ethanol, we need to incorporate the amount of water, selectivity of ethylene and conversion of Ethanol too.

For every 100 kmol of feed, according to 95% v/v Ethanol, we have

85.43 kmol of Ethanol

14.57 kmol of Water

Also, conversion of ethanol over Nano- HZSM 5 = 92%

Selectivity of ethylene over Nano- HZSM 5 = 98.69%

Incorporating all these factors, for producing 90 kmol of Ethylene, we need

= ((90/ (0.992*0.9869))/85.43) *100

≈110 kmols/hr of feed

Basis = 1 hr of feed

4.2 Fixed bed tubular reactor

The feed undergoes a series of reactions in the fixed bed tubular reactor where ethylene and a number of various by-products are formed. The inlet feed composition is given as follows along with the reaction set.

Table 5 Reactor feed composition

Reactor Inlet		
Feed	110	kmol
Ethanol	93.973	kmol
	4322.758	kg
Water	16.027	kmol
	288.486	kg

The reaction set is as follows:

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$

$$2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O$$

$$C_2H_5OH \rightarrow C_2H_4O + H_2$$

$$2C_2H_5OH \rightarrow C_2H_6 + 2CO + H_2$$

$$3C_2H_5OH \rightarrow 2C_3H_6 + 3H_2O$$

$$2C_2H_5OH \rightarrow C_4H_8 + 2H_2O$$

$$5C_2H_5OH \rightarrow 2C_5H_{10} + 3H_2O$$

$$7C_2H_5OH \rightarrow 2C_7H_{14} + 7H_2O$$

By using the following formula and respective selectivities, the following table was calculated:

$$Product\ (kg) = \frac{Moles\ of\ ethanol * Conversion * Selectivity * MW}{Stiochiometric\ factor}$$

Table 6 Reactor material balance

Component	Feed (kg)	Selectivity	Product (kg)	Mass Fraction
Ethanol	4322.758	-	34.582	0.00750
Water	288.486	-	1964.370	0.42600
Hydrogen	0	0	0.233	0.00005
Carbon monoxide	0	0	1.305	0.00028
Ethylene	0	0.9869	2576.001	0.55863
Ethane	0	0.0005	0.699	0.00015
Propene	0	0.0041	10.702	0.00232
Butene	0	0.0045	11.746	0.00255
Acetaldehyde	0	0.0005	2.051	0.00044
Pentene	0	0.0015	3.915	0.00085
Diethyl Ether	0	0.0005	1.725	0.00037
Heptene	0	0.0015	3.915	0.00085
Total	**4611.244**	**1**	**4611.244**	**1**

4.3 Vertical Knock out Drum

The product then passes into a vertical knock out drum having an efficiency of 90%. It means that 90% of the liquid in separator feed would be removed in bulk form while the 10% would be taken from the top stream as carryover.

At the conditions of 1.5 bars and 30℃, the following components are in liquid phase:

Ethanol, water, diethyl ether, pentene, heptene and acetaldehyde

For the carryover of liquid, we used the following formula of efficiency:

$$E = \frac{F-C}{F} \text{ x } 100$$

Where,

E = Efficiency of separator = 90%

F = Liquid in feed = 2010.56 kgs

C = Carryover of liquid in the gas stream

Putting above values in the equation,

$$C = 201.56 \text{ kg}$$

After this, the following calculations were done:

Table 7 Liquid phase entering Knock out drum

Liquid phase (kg)			
Water	1964.370	196.437	1767.933
Ethanol	34.582	3.458	31.124
Acetaldehyde	2.051	0.205	1.846
Pentene	3.915	0.392	3.524
Diethyl Ether	1.725	0.172	1.552
Heptene	3.915	0.392	3.524
Total	2010.559	201.056	1809.503

Table 8 Knock out drum material balance

Component	**Inlet (kg)**	**Top (kg)**	**Bottom (kg)**
Ethanol	34.582	3.4582064	31.124
Water	1964.370	196.437041	1767.933
Hydrogen	0.233	0.233	0.000
Carbon monoxide	1.305	1.305	0.000
Ethylene	2576.001	2576.001	0.000
Ethane	0.699	0.699	0.000
Propene	10.702	10.702	0.000
Butene	11.746	11.746	0.000
Acetaldehyde	2.051	0.205	1.846
Pentene	3.915	0.392	3.524
Diethyl Ether	1.725	0.172	1.552
Heptene	3.915	0.392	3.524
Total	**4611.244**	**2801.741**	**1809.50266**

4.4 Gasunie Cyclone

This separator is designed for an efficiency of almost 100%.

So, all the liquid entrained as a carryover in previous separator will be removed through this separator.

According to this, we get the following balance of Gasunie cyclone:

Table 9 Gasunie cyclone material balance

Component	Inlet (kg)	Top (kg)	Bottom (kg)
Ethanol	3.458	0.000	3.458
Water	196.437	0.000	196.437
Hydrogen	0.233	0.233	0.000
Carbon monoxide	1.305	1.305	0.000
Ethylene	2576.001	2576.001	0.000
Ethane	0.699	0.699	0.000
Propene	10.702	10.702	0.000
Butene	11.746	11.746	0.000
Acetaldehyde	0.205	0.000	0.205
Pentene	0.392	0.000	0.392
Diethyl Ether	0.172	0.000	0.172
Heptene	0.392	0.000	0.392
Total	**2801.741**	**2600.685**	**201.056**

4.5 Cryogenic Distillation Column

The balance on distillation column was done using Hengstebeck method.

The following data was used:

Table 10 Required data for distillation column

Component	BP (℃)	α_{av}
Hydrogen	-259.2	361.4152
Carbon monoxide	-191.5	256.2924
Ethylene (LK)	-103.7	1.8706
Ethane (HK)	-89	1.0000
Propene	-47.6	0.1483
Butene	-6.3	0.0205
Acetaldehyde	20.2	0.0049
Pentene	30	0.0032
Diethyl Ether	34.6	0.0022
Heptene	94	0.0001

The balance obtained by using the relative volatilities was as follows:

Table 11 Distillation column material balance

Component	Feed (kg)	Top (kg)	Bottom (kg)
Ethanol	0.00	0.00	0.00
Water	0.00	0.00	0.00
Hydrogen	0.23	0.23	0.00
Carbon monoxide	1.31	1.31	0.00
Ethylene	2576.00	2550.5	25.50
Ethane	0.70	0.20	0.50
Propene	10.70	0.00	10.70
Butene	11.75	0.00	11.75
Acetaldehyde	0.21	0.00	0.21
Pentene	0.39	0.00	0.39
Diethyl Ether	0.17	0.00	0.17
Heptene	0.39	0.00	0.39
Total	**2601.85**	**2552.23**	**49.61**

The purity achieved for Ethylene was 99.98%.

5 Energy Balance

Energy balance was applied on the following equipments:

5.1 Pump

The first pump is being used to provide a head so that the feed can flow. The discharge pressure is 1.5 bar.

Specific volume of ethanol = 1003 cm^3/kg

Specific volume of water = 1267.43 cm^3/kg

Hence, average specific volume = (0.936*1003) +(0.064*1267.43)

= 1019.92 cm^3/kg

The volume expansivity can be calculated as 0.00103.

The isentropic work can be calculated as,

= ((1019.92) *(150-100))/1000000

= 0.051 kJ/kg

Taking isentropic efficiency = 75%

$$Actual\ Work = \frac{W_s}{\eta}$$

= 0.068 kJ/kg

As, feed flowrate = 4611 kg

Actual work = 0.068*4611 kJ

= 313.54 kJ

Hence, Power = $\frac{313.54}{3600}$ = 0.087 kW

5.2 Heat Exchangers

5.2.1 HE – 01

By using, $Q = mC_p\Delta T$ and the overall calculation for the exit temperature of feed was done.

Reference Temp = 25℃

Table 12 Energy balance on HE-01

	Pressure (bar)	**Temperature ℃**	**Cp (kJ/kg. ℃)**	**m (kg)**	**Q (kJ)**
Product in	1.5	240	2.13	3227.8708	1472324.39
Product out	1.5	90	2.56	3227.8708	536988.985
Feed in	1.5	25	3.356	4611.244	0
Feed out	1.5	**85.44**	3.356	4611.244	935335.401

5.2.2 HE – 02

Same equations are applied to calculate the mass flowrate of steam.

Table 13 Energy balance on HE-02

	Pressure (bar)	**Temperature ℃**	**Cp (kJ/kg. ℃)**	**m (kg)**	**Q (kJ)**
Steam in	5	400	2.069	3831.94	2974345.3
Stream out	4.7	255	2.048	3831.94	1804996.6
Feed in	3	85.44	3.356	4611.24	935335.40
Feed out	3	240	2.097	4611.24	2079341.8

5.2.3 HE – 03

To find out the cooling water outlet temperature by same equation.

Table 14 Energy balance on HE-03

	Fraction	**Pressure (bar)**	**Temperature (℃)**	**Cp (kJ/kg. ℃)**	**m (kg)**	**Q (kJ)**
Product in	0.3	3	240	2.12152866	1383.3732	630996.166
Product out	0.3	3	90	2.55938652	1383.3732	230138.137
CW in	1	1	25	4.18	7930.14641	0
CW out	1	1	**37.09**	4.18	7930.14641	400858.029

5.2.4 HE – 04

To find cooling water mass flowrate by same equation.

Table 15 Energy balance on HE-04

	Pressure (bar)	**Temperature (℃)**	**Cp (kJ/kg. ℃)**	**m (kg)**	**Q (kJ)**
CW in	1	15	4.18	**7930.146**	-331480.12
CW out	1	25	4.18	7930.146	0
Product in	3	90	2.55938651	4611.244	767127.12
Product out	3	60	2.69928401	4611.244	435647.00

5.3 Reactor

$$Q = \Delta H_{products} - \Delta H_{reactants}$$

Table 16 Reactor energy balance

	$\Delta \boldsymbol{H}_{\boldsymbol{products}}$		$\Delta \boldsymbol{H}_{\boldsymbol{reactants}}$
Fraction	0.7	0.3	1
Temperature ℃)	240	240	240
Pressure (bar)	3	3	3
Cp (kJ/kg. ℃)	2.12152866	2.12152866	2.09734236
m (kg)	3227.8708	1383.3732	4611.244
H (kJ)	1472324.39	630996.166	2079341.84

Energy required = 23978.7 kJ

5.4 Vertical Knock out Drum

By same equation, $Q = mC_p\Delta T$

Table 17 Knock out drum energy balance

	Inlet	**Top**	**Bottom**
Temperature	30	30	30
Pressure (bar)	1.5	1.5	1.5
Cp (kJ/kg. ℃)	2.694	1.68	4.18
m (kg)	4611.244	2701.21	1910.03
Q (kJ)	62113.45668	22604.92	39930.56

The inlet energy is almost equal to the total of outlet.

5.5 Distillation Column

The energy balance on streams of distillation column is as follows:

Table 18 Distillation column energy balance

	Feed	**Top**	**Bottom**
Temperature (℃)	-28	-29.5	-29
Pressure (bar)	22	21.96	21.99
Cp (kJ/kg. ℃)	1.38	1.38	2.5398103
m (kg)	2590.11	2552.23369	37.8735176
Q (kJ)	-257618.9	-260592.79	-7070.0789

6 Equipment Design

Design calculations for the major equipments in the process flow diagram are described below.

6.1 Isothermal Fixed Bed Tubular Reactor

The reactor we have chosen is an isothermal tubular fixed bed reactor.

Tubes of length 8 m and diameter 3.175 cm, are filled with a zeolite catalyst, with a WHSV (weight hourly space velocity) of $1h^{-1}$.

We know that weight hourly space velocity is given by

$$\text{WHSV} = \frac{Weight\ of\ feed\ flowing\ per\ hour}{Weight\ of\ the\ catalyst}$$

For Nano-cat WHSV $= 1h^{-1}$

Weight of feed flowing per hour = 4611 kg

By plugging in the value of feed flowing, we get the weight of the catalyst

$$\text{Weight of the catalyst} = 4611\text{kg}$$

The density of the catalyst = 2.5*10^3 kg/m^3

The volume of the catalyst would be =1.84 m^3

Now,

Number of Tubes required

$$n_{tubes} = \frac{Volume\ of\ the\ catalyst}{Volume\ of\ the\ tubes} = \frac{1.84\ m^3}{6.33 * 10^{-3}\ m^3} = 291$$

$$A_{tubes} = n_{tubes}.\pi r_{tube}^2$$

There has to be a distance between the tubes, assuming a packing factor

$$Pf_{tube} = 0.25$$

Area inclusive of packing factor would be

$$A_{reactor} = \frac{n_{tubes}.A_{tubes}}{Pf_{tube}} = \frac{291 * 0.23\ m^2}{0.25} = 267.72\ m^2$$

$$d_{reactor} = \sqrt{\frac{4A_{reactor}}{\pi}}$$

$$= \sqrt{\frac{2.452\ m^2}{\pi}} = 18.46 \text{ m}$$

In industrial scale plant a guard bed is usually required to remove impurities

$$V_{guard\ bed} = 0.2 V_{catalyst}$$

$$V_{guard\ bed} = 0.2(1.84\ m^3) = 0.368\ m^3$$

$$h_{guard\ bed} = \frac{V_{gb}}{A_{tubes}}$$

$$= \frac{0.368\ m^3}{0.23\ m^2} = 1.6 \text{ m}$$

The height of reactor would be given by

$$h_{reactor} = h_{tube} + h_{guard\ bed} + (0.5m * 2)$$

By plugging in the values, we get,

$$h_{reactor} = 10.6\ m$$

$$V_{reactor} = A_{reactor} . h_{reactor} = 2838\ m^3$$

The following table shows the reactor design summary specifications.

Table 19 Reactor specification sheet

Parameter	**Specifications**
Weight of Catalyst	*4611 kgs*
Volume of Catalyst	*1.84* m^3
No. of Tubes	*868*
Height of Guard Bed	*1.6 m*
Area of Reactor	*267.72* m^2
Height of Reactor	*10.6 m*
Diameter of Reactor	*18.46 m*
Volume of Reactor	2838 m^3

6.2 Vertical Knockout Drum

This vertical separator has Efficiency of 90%.

The settling velocity is given by:

$$u_s = 0.0105 \left[{(\rho_L - \rho_g)} \middle/ {\rho_g} \right]^{1/2}$$

$$u_s\text{=0.26 m/s}$$

Now, Diameter for Vertical Knock Out Drum is given by the equation:

$$D_V = \sqrt{4V_V / \pi u_s}$$

Putting values gives,

$$D = 1.5\ m$$

Now,

L/D ratio of separators is between 3-5.

Taking, L/D = 3.5,

L = 3.5 D

L = 5.4 m

Pressure drop is given by

$$\Delta P = 0.5\ \rho_m v_{m,\,in}^2 + 0.22\ \rho_g v_{g,\,out}^2$$

$$\Delta P = 1.8\ kPa$$

6.3 Cyclone with straight inlet and swirler: Gasunie Cyclone

This separator has an efficiency >99%.

First, we find the volumetric gas load factor by

$$Q_{max}^* = Q_{G,max} \sqrt{\rho_g / (\rho_L - \rho_g)}$$

where

Q^*_{max} = Volumetric gas load factor, ${m^3}/{s}$

$Q_{G,max}$ = Highest gas flowrate possible at inlet, 0.4963 ${m^3}/{s}$

ρ_g= Gas density at inlet, 1.674 ${kg}/{m^3}$

ρ_L= Liquid density at inlet, 999.9 ${kg}/{m^3}$

By putting values and doing calculations,

$$Q^*_{max} = 0.021\ {m^3}/{s}$$

Now, diameter of separator is given by

$$D \geq 1.19\sqrt{Q^*_{max}}$$

$$\mathrm{D = 0.36\ m}$$

For Diameter of cyclone:

$$D \geq \left\{3360\ \rho_g\ Q^2_{G,\mathrm{max}}\ /\pi^2 \Delta P_{max}\right\}^{0.25}$$

$$\Delta P_{max} = 46.8\ kPa \text{ (to keep downstream at 1 atm)}$$

Putting values,

Diameter of cyclone = 0.23 m

Now,

Total minimum height of cyclone separator = 4.2 D

Taking 4.5D gives,

L = 1.2 m

Table 20 Separators specification sheet

Parameters	**Vertical Knock out Drum**	**Gasunie Cyclone**
Diameter of Separator	*1.5 m*	*0.36 m*
Diameter of Cyclone	-----	*0.23 m*
Height of Separator	*5.4 m*	*1.2 m*
Pressure Drop	*1.8 kPa*	*46.8 kPa*
Efficiency	*90%*	*>99%*

6.4 Cryogenic Distillation Column

The following is the detailed flow of all components at the inlet of the distillation column:

Table 21 Flow composition at column inlet

Component	Molar Flow (kmol)			Mole Fractions		
	Feed	Top	Bottom	Feed	Top	Bottom
Hydrogen	0.231	0.117	0.114	0.0025	0.0013	0.0798
Carbon Monoxide	0.0466	0.046	9.4E-05	0.0005	0.0005	6.59E-05
Ethylene (LK)	91.836	91	0.836	0.9917	0.9981	0.5859
Ethane (HK)	0.023	1.00E-02	0.013	0.0003	0.0001	0.0093
Pentene	0.254	9.07E-25	0.254	0.0027	9.94E-27	0.1783
Butene	0.209	8.91E-39	0.209	0.00243	9.77E-41	0.1467
Total	92.600	91.173	1.427	1	1	1

By using Hengstebeck method,

Table 22 Hengstebeck method values

Component	α_i	$\alpha_i x_{i,f}$	$\alpha_i x_{i,d}$	$\sum \frac{\alpha_i x_{i,f}}{\alpha_i - \theta} = 1 - q$	$\sum \frac{\alpha_i x_{i,d}}{\alpha_i - \theta} = R_m + 1$
Hydrogen	666.833	1.665	0.858	0.0025	0.0013
Carbon Monoxide	30.867	0.015	0.016	0.0005	0.0005
Ethylene (LK)	1.722	1.707	1.718	2.3663	2.3815
Ethane (HK)	1	0.0002	0.0001	-1.3215	-0.5484
Propene	0.248	0.0007	2.47E-27	-0.0009	-3.3E-27
Butene	0.056	0.0001	5.44E-42	-0.0001	-5.8E-42
				1.0468	1.8349

$$N_m = \frac{\ln[\frac{x_{LK}}{x_{HK}}]_d [\frac{x_{HK}}{x_{LK}}]_b}{ln\alpha_{LK}}$$

By plugging the values, we get

$$N_m = 9$$

For Minimum Reflux Ratio

$$\sum \frac{\alpha_i x_{i,f}}{\alpha_i - \theta} = 1 - q$$

$$\sum \frac{\alpha_i x_{i,d}}{\alpha_i - \theta} = R_m + 1$$

Since our feed is saturated vapor

$$q = 0$$

$$\sum \frac{\alpha_i x_{i,f}}{\alpha_i - \theta} = 1$$

$$R_m + 1 = 1.83$$

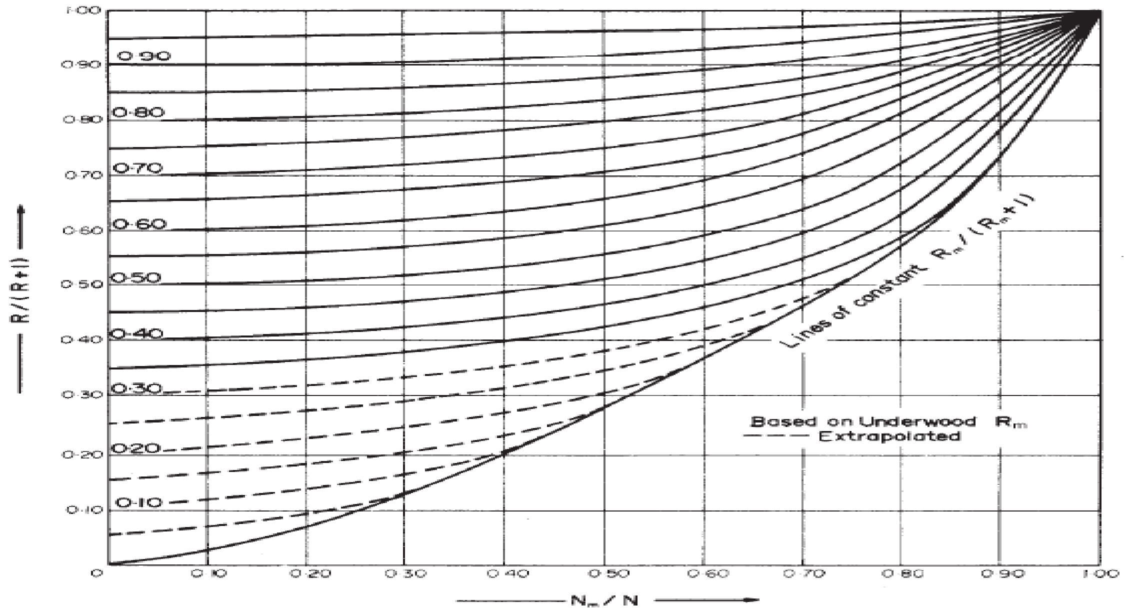
$$R_m = 0.83$$

$$\frac{R_m}{R_m+1} = 0.45$$

For an actual Reflux ratio of R = 4

$$\frac{R}{R+1} = 0.8$$

By Erbar-Maddox Correlation,



Erbar-Maddox correlation (Erbar and Maddox, 1961)

Figure 6.1 Erbar- Maddox correlation graph

$$\frac{N_m}{N} = 0.89$$

As,

$$N_m = 9$$

The number of ideal stages would be

$$N = 11$$

Number of Ideal stages excluding the reboiler, N = 10

6.4.1 Feed Point Location

By Kirkbride equation,

$$log\left[\frac{N_r}{N_s}\right] = 0.206\ log\left[\left(\frac{B}{D}\right)\left(\frac{x_{f,HK}}{x_{f,LK}}\right)\left(\frac{x_{b,LK}}{x_{d,HK}}\right)^2\right]$$

By plugging in the values and solving the equation, we get

$$N_s = 5.81 \cong 6$$

6.4.2 Overall Column Efficiency

By O'Connell correlation equation, we have

$$E_o = 51 - 32.5\ log(\alpha_{average}\mu_{average})$$

$$E_o = 51 - 32.5\ log((1.73)(0.064)) = 82\%$$

So, the actual number of trays

$$N_{actual} = \frac{10}{0.82} = 14$$

6.4.3 Flooding Velocity

$\rho_{Liquid} = 439\ kg/m^3$ $\rho_{Gas} = 42\ kg/m^3$

σ = Surface tension= 4 dyne/cm

G = 2577kg/hr L= 24.4 kg/hr

$$U_f = C\left(\frac{\rho_{Liquid} - \rho_{Gas}}{\rho_{Gas}}\right)^{0.5}$$

Where C = Capacity factor

$$C = C_{SB} F_{St} F_F F_{HA}$$

- For 1-foot tray spacing, from flooding correlation graph

$$C_{SB} = 0.2 \text{ ft/s} = 119 \text{ m/hr}$$

$$F_{LG} = \frac{L}{G}\left(\frac{\rho_{Gas}}{\rho_{Liquid}}\right)^{0.5}$$

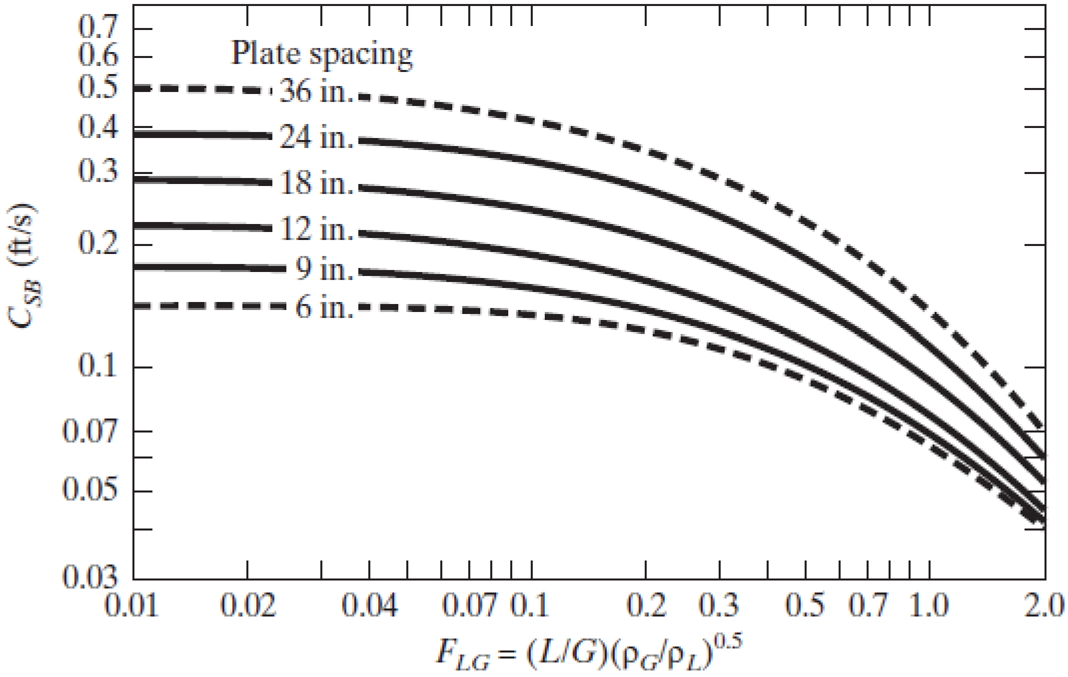


Figure 6.2 Flooding correlation graph

Surface Tension Factor = $F_{St} = \left(\frac{\sigma}{20}\right)^{0.20} = \left(\frac{4\ dyne/cm}{20}\right)^{0.20} = 0.724$

The Hole area factor F_{HA} is 1

$Since, \frac{A_h}{A_a} > 0.10$ (as we would be taking this ratio to be 0.12)

Assuming a Foaming factor of 0.75 for the system

After finding the values of capacity factor, and plugging it into equation (Eq. – 6.21)

We get the superficial velocity to be

$$U_f = 119\ m/hr\left(\frac{439\ kg/m^3 - 42\ kg/m^3}{42\ kg/m^3}\right)^{0.5}$$

$$U_f = 366 \text{ m/hr}$$

6.4.4 Tower Inside Diameter

$$D_c = \sqrt{\frac{4G}{fU_f\pi\rho_{Gas}\left(1-\frac{A_d}{A_T}\right)}}$$

$$\frac{A_d}{A_T} = 0.1 \text{ as } F_{LV} < 0.1$$

$Fraction\ for\ downcomer\ = f = 0.85$

$$D_c = 0.53\ m$$

6.4.5 Tower Height

$$h_c = N_R s_t$$

$$= 14 \text{ (1 ft)} = 14 \text{ ft} = 4.26 \text{ m}$$

6.4.6 Plate Design (Sieve Trays)

Column Diameter$= D_c = 0.53\ m$

Column Area $= A_c = 0.22\ m^2$

Downcomer Area $= A_d = 0.033\ m^2$ (15% of column area)

Net Area $= A_n = A_c - A_d = 0.187 m^2$

Active Area $= A_a = A_c - 2A_d = 0.154\ m^2$

Hole Area $= A_h = 0.015\ m^2$

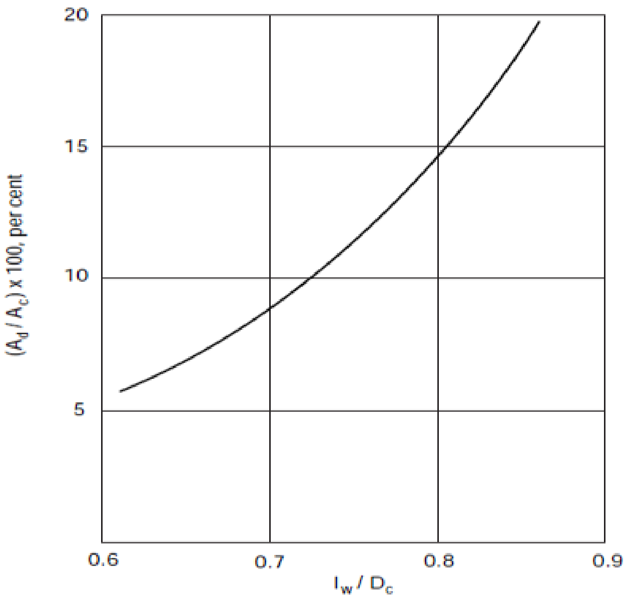


Figure 6.3 Graph for weir length

Weir Length= $l_w = 0.424$ m

Plate thickness $= 5\ mm$

Weir height $= h_w = 50\ mm$

Hole diameter $= D_h = 5mm$

Area of one hole = 1.96*$10^{-5}m^2$

Number of Holes = 765

6.4.7 Pressure Drop Across the Plate

$$h_D = \left[\frac{\hat{u}_v}{C_0}\right]^2 \frac{\rho_{gas}}{\rho_{liquid}}$$

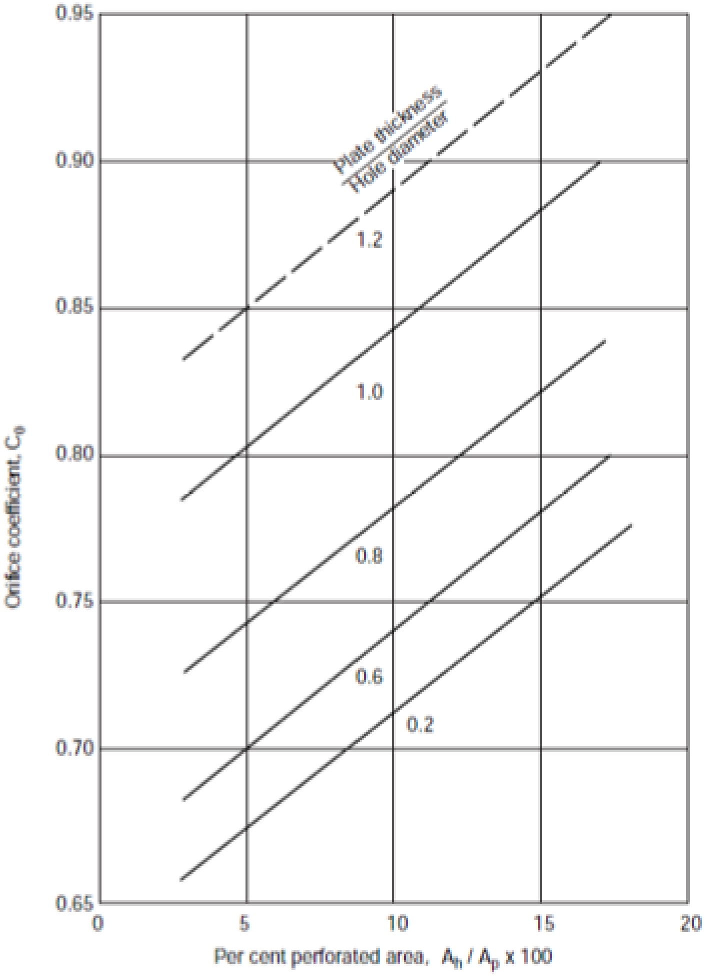


Figure 6.4 Discharge coefficient, sieve plates

$$C_0 = 0.83$$

$$\hat{u}_v = 0.58$$

By putting values, we get

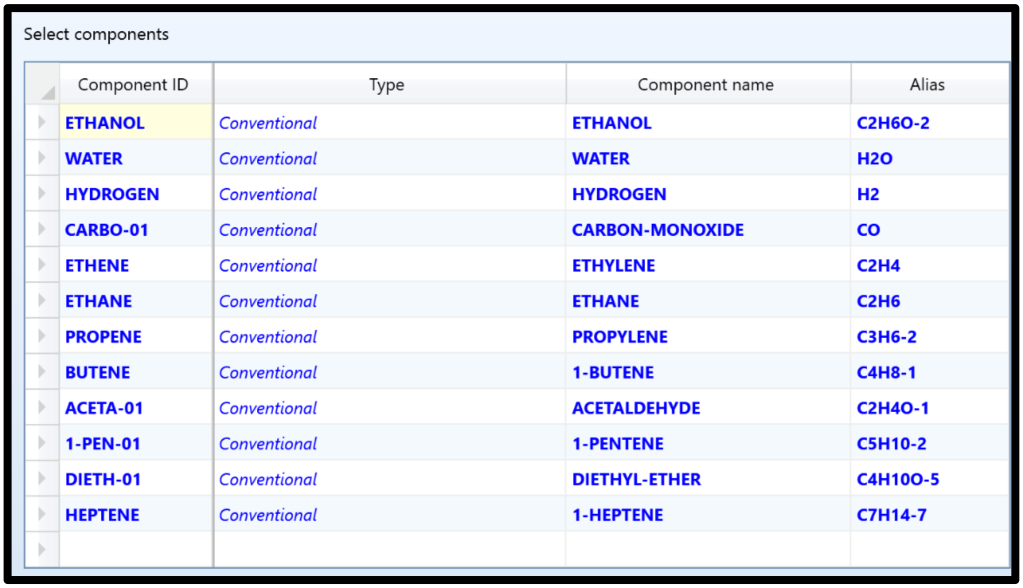
$$h_D = 2.3 \text{ mm}$$

Table 23 Distillation column specification sheet

Parameters	**Specifications**
Minimum No. of Stages	*9*
Minimum Reflux Ratio	*0.83*
Actual Reflux Ratio	*4*
No. of Ideal Stages with Reboiler	*11*
Feed Point Location	*6*
Overall Column Efficiency	*82%*
Actual Number of Trays	*14*
Flooding Velocity	*366 m/hr*
Column Inside Diameter	*0.53 m*
Column Height	*4.26 m*
Type of trays	*Sieve*
Weir length	*0.424 m*
Weir height	*50 mm*
Plate thickness	*5 mm*
No. of holes	*765*
Pressure drop across plate	*2.3 mm*

7 Simulation

The simulation was done on Aspen Plus. Stoichiometric reactor was used, the results obtained were pretty close with the values which were calculated through material and energy balance and equipment design. The purity finally obtained was 99.8%. Sensitivity analysis was also performed on the distillation column and its results indicated that the process was pretty close to optimization. The following figure shows the components added.

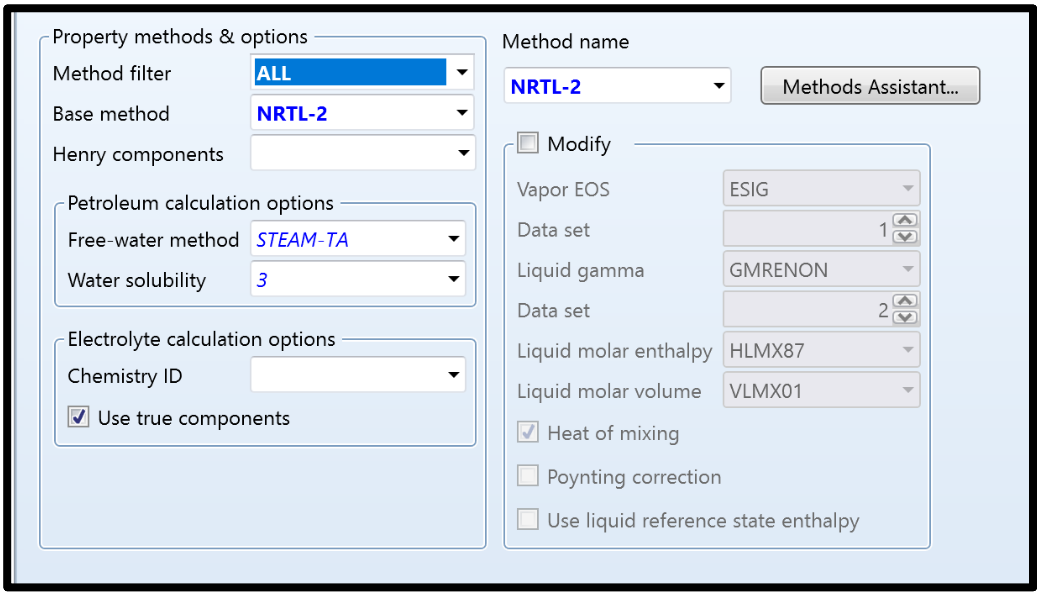


Select components

Component ID	Type	Component name	Alias
ETHANOL	Conventional	ETHANOL	C2H6O-2
WATER	Conventional	WATER	H2O
HYDROGEN	Conventional	HYDROGEN	H2
CARBO-01	Conventional	CARBON-MONOXIDE	CO
ETHENE	Conventional	ETHYLENE	C2H4
ETHANE	Conventional	ETHANE	C2H6
PROPENE	Conventional	PROPYLENE	C3H6-2
BUTENE	Conventional	1-BUTENE	C4H8-1
ACETA-01	Conventional	ACETALDEHYDE	C2H4O-1
1-PEN-01	Conventional	1-PENTENE	C5H10-2
DIETH-01	Conventional	DIETHYL-ETHER	C4H10O-5
HEPTENE	Conventional	1-HEPTENE	C7H14-7

Figure 7.1 Components added on Aspen Plus

The following shows the property package selected and reactions.



Property methods & options

Method filter: ALL

Base method: NRTL-2

Henry components:

Petroleum calculation options

Free-water method: STEAM-TA

Water solubility: 3

Electrolyte calculation options

Chemistry ID:

☑ Use true components

Method name: NRTL-2

☐ Modify

Vapor EOS: ESIG

Data set: 1

Liquid gamma: GMRENON

Data set: 2

Liquid molar enthalpy: HLMX87

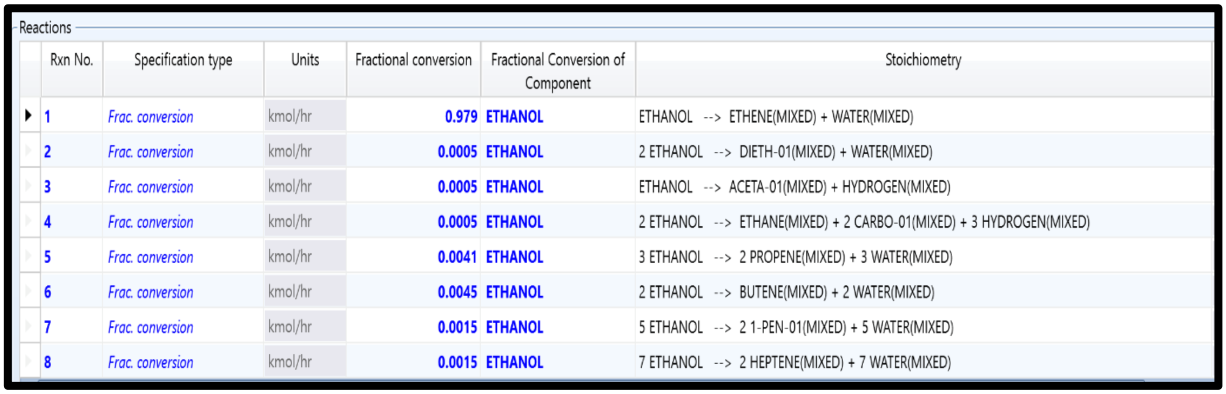
Liquid molar volume: VLMX01

☑ Heat of mixing

☐ Poynting correction

☐ Use liquid reference state enthalpy

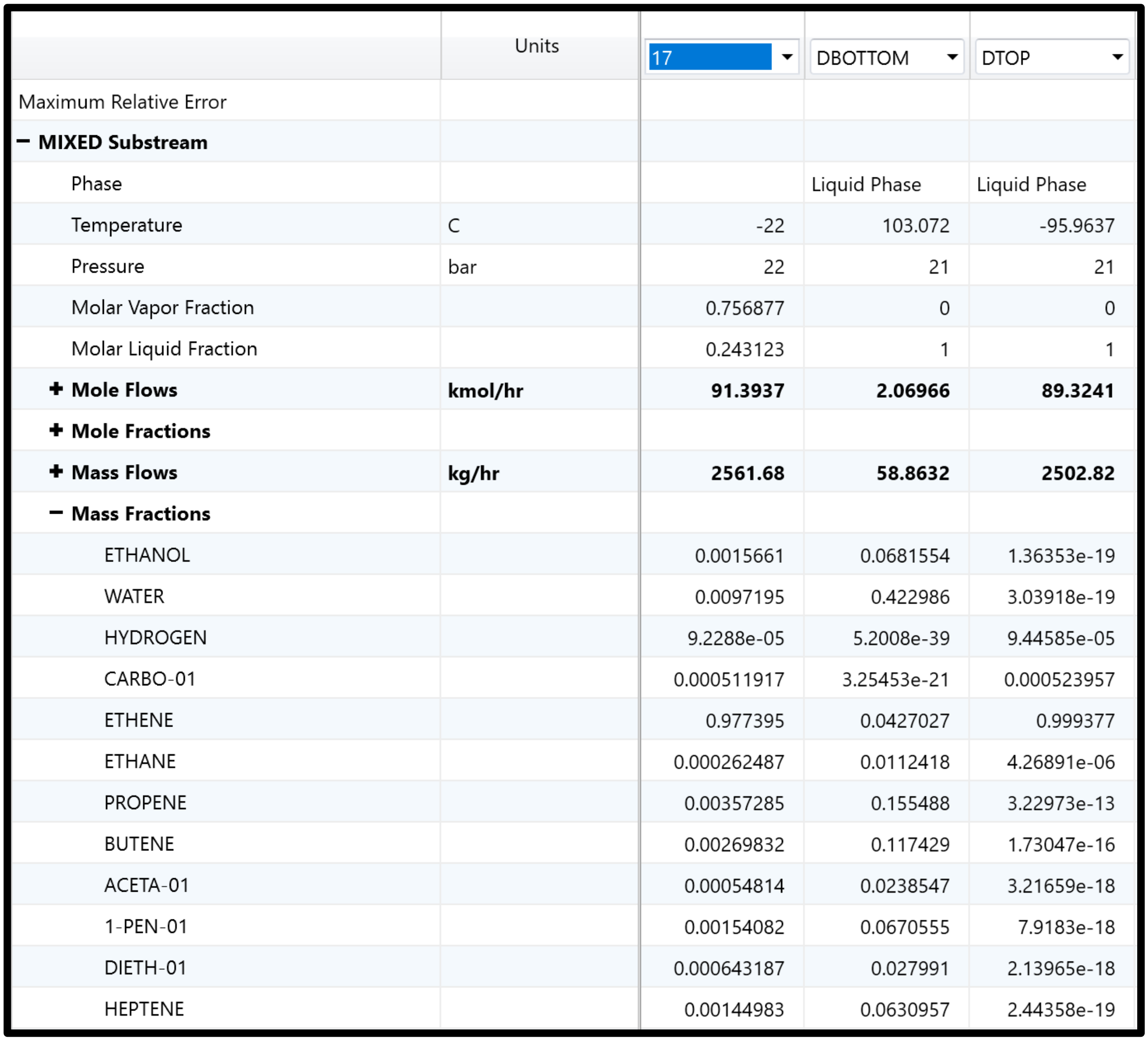
Figure 7.2 Property package on Aspen Plus



Reactions

Rxn No.	Specification type	Units	Fractional conversion	Fractional Conversion of Component	Stoichiometry
1	Frac. conversion	kmol/hr	0.979	ETHANOL	ETHANOL --> ETHENE(MIXED) + WATER(MIXED)
2	Frac. conversion	kmol/hr	0.0005	ETHANOL	2 ETHANOL --> DIETH-01(MIXED) + WATER(MIXED)
3	Frac. conversion	kmol/hr	0.0005	ETHANOL	ETHANOL --> ACETA-01(MIXED) + HYDROGEN(MIXED)
4	Frac. conversion	kmol/hr	0.0005	ETHANOL	2 ETHANOL --> ETHANE(MIXED) + 2 CARBO-01(MIXED) + 3 HYDROGEN(MIXED)
5	Frac. conversion	kmol/hr	0.0041	ETHANOL	3 ETHANOL --> 2 PROPENE(MIXED) + 3 WATER(MIXED)
6	Frac. conversion	kmol/hr	0.0045	ETHANOL	2 ETHANOL --> BUTENE(MIXED) + 2 WATER(MIXED)
7	Frac. conversion	kmol/hr	0.0015	ETHANOL	5 ETHANOL --> 2 1-PEN-01(MIXED) + 5 WATER(MIXED)
8	Frac. conversion	kmol/hr	0.0015	ETHANOL	7 ETHANOL --> 2 HEPTENE(MIXED) + 7 WATER(MIXED)

Figure 7.3 Reaction set on Aspen Plus



	Units	17	DBOTTOM	DTOP
Maximum Relative Error				
− MIXED Substream				
Phase			Liquid Phase	Liquid Phase
Temperature	C	-22	103.072	-95.9637
Pressure	bar	22	21	21
Molar Vapor Fraction		0.756877	0	0
Molar Liquid Fraction		0.243123	1	1
+ Mole Flows	**kmol/hr**	**91.3937**	**2.06966**	**89.3241**
+ Mole Fractions				
+ Mass Flows	**kg/hr**	**2561.68**	**58.8632**	**2502.82**
− Mass Fractions				
ETHANOL		0.0015661	0.0681554	1.36353e-19
WATER		0.0097195	0.422986	3.03918e-19
HYDROGEN		9.2288e-05	5.2008e-39	9.44585e-05
CARBO-01		0.000511917	3.25453e-21	0.000523957
ETHENE		0.977395	0.0427027	0.999377
ETHANE		0.000262487	0.0112418	4.26891e-06
PROPENE		0.00357285	0.155488	3.22973e-13
BUTENE		0.00269832	0.117429	1.73047e-16
ACETA-01		0.00054814	0.0238547	3.21659e-18
1-PEN-01		0.00154082	0.0670555	7.9183e-18
DIETH-01		0.000643187	0.027991	2.13965e-18
HEPTENE		0.00144983	0.0630957	2.44358e-19

Figure 7.4 Distillation column stream results on Aspen Plus

The simulation is shown below.

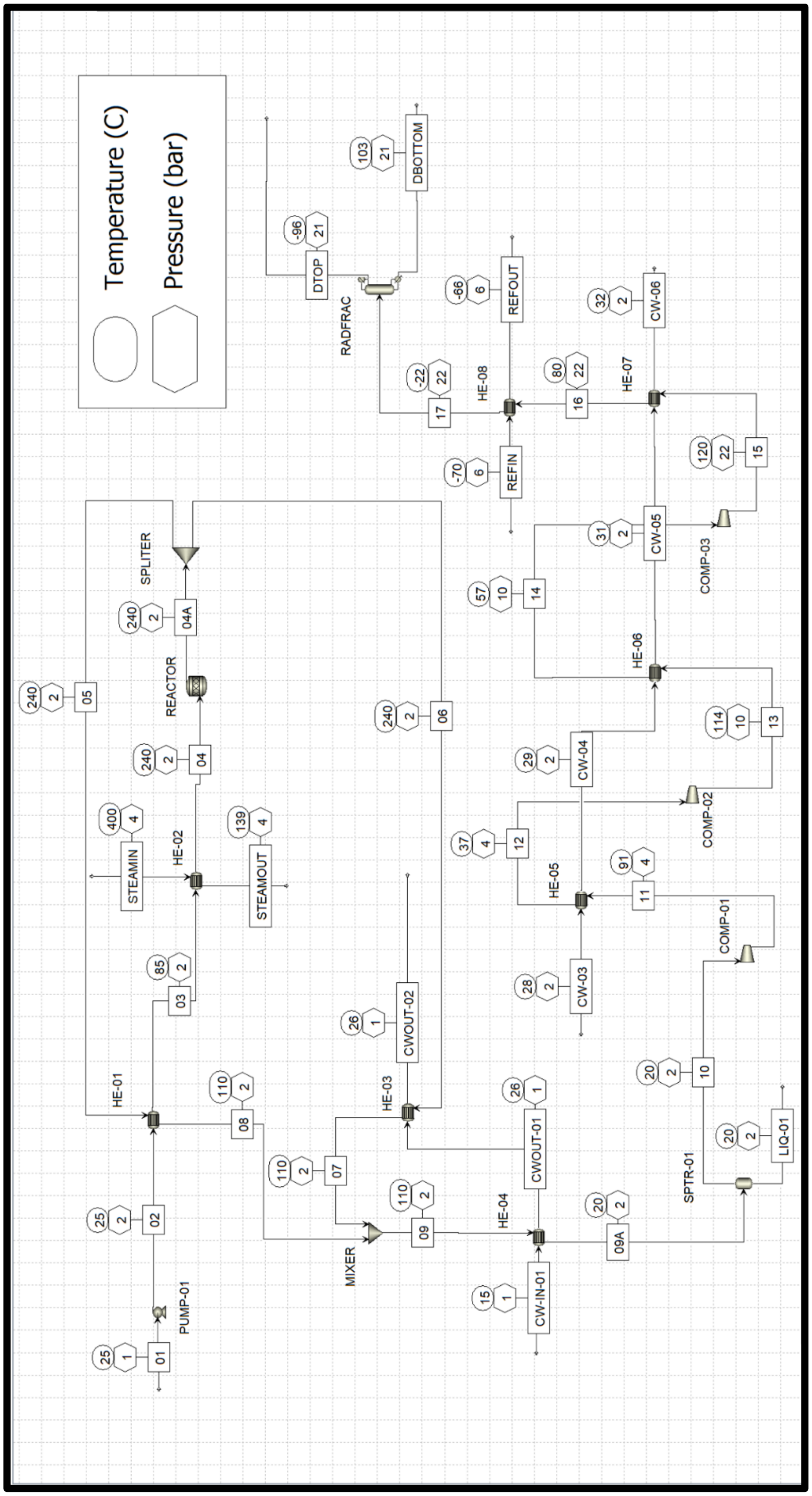
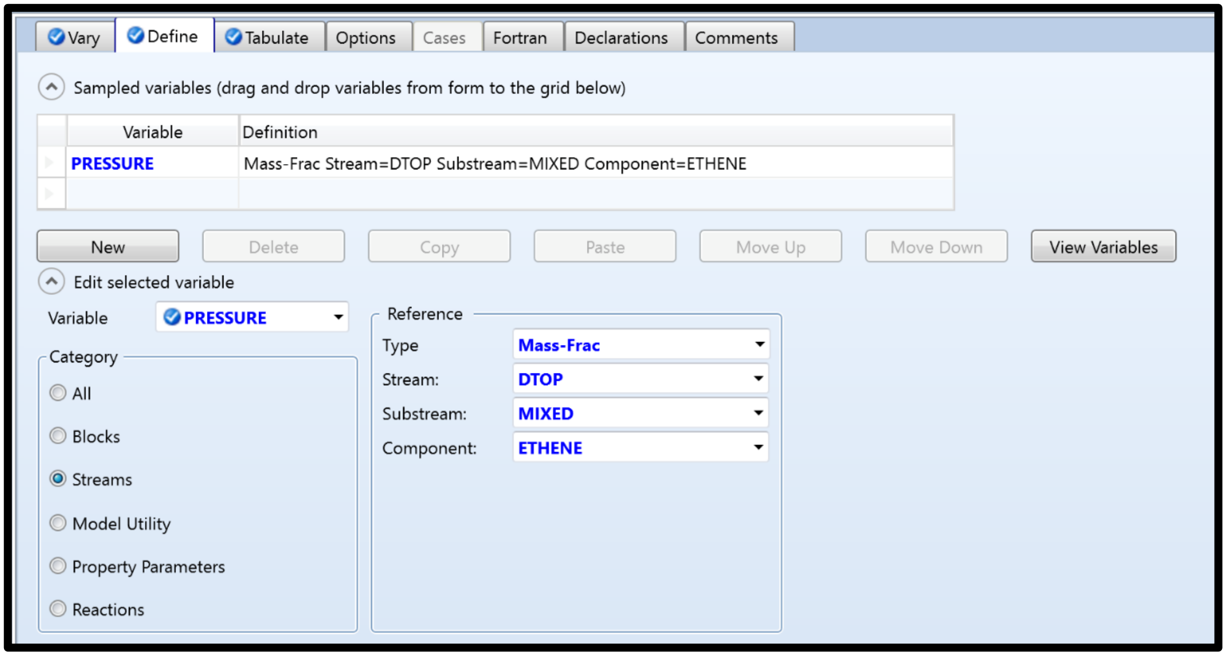


Figure 7.5 Process simulation on Aspen Plus

A sensitivity analysis was done on the distillation column feed temperature and pressure and its effect on purity of Ethylene.



Sampled variables (drag and drop variables from form to the grid below)

Variable	Definition
PRESSURE	Mass-Frac Stream=DTOP Substream=MIXED Component=ETHENE

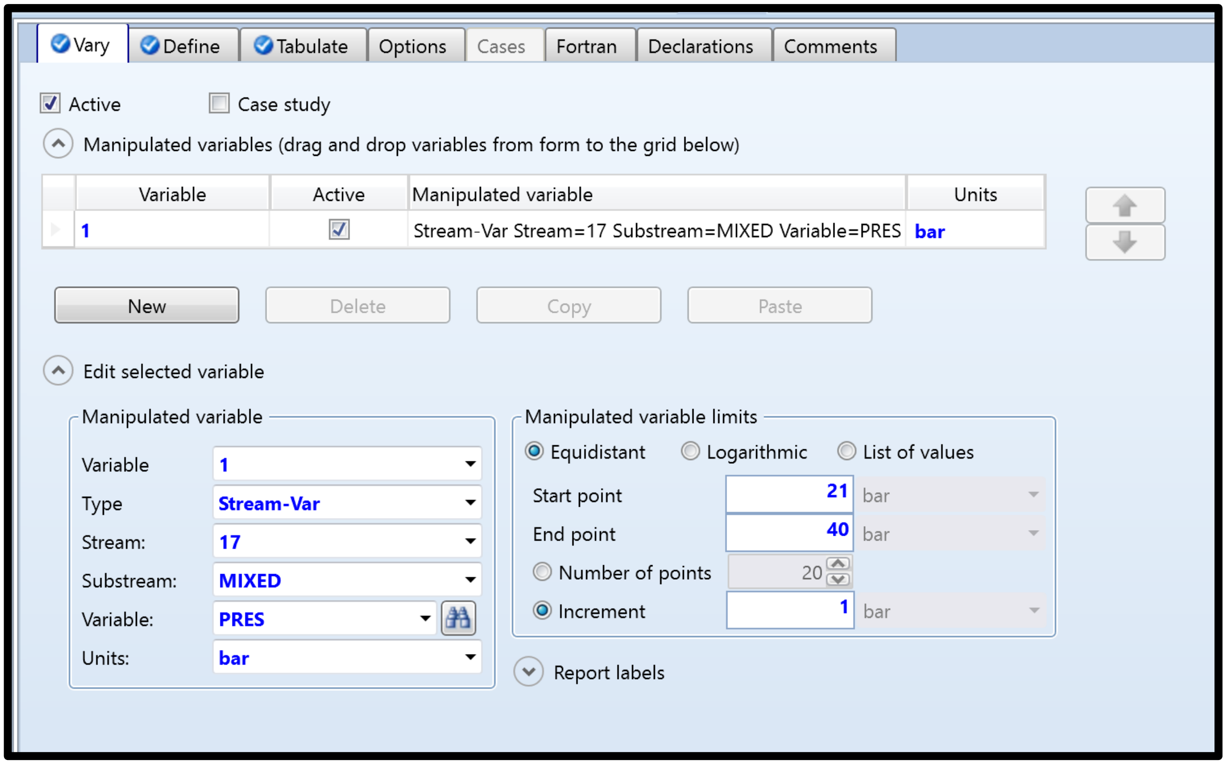
Edit selected variable

Variable: PRESSURE

Category
○ All
○ Blocks
● Streams
○ Model Utility
○ Property Parameters
○ Reactions

Reference
Type: Mass-Frac
Stream: DTOP
Substream: MIXED
Component: ETHENE

Figure 7.6 Sensitivity analysis independent variable



☑ Active ☐ Case study

Manipulated variables (drag and drop variables from form to the grid below)

Variable	Active	Manipulated variable	Units
1	☑	Stream-Var Stream=17 Substream=MIXED Variable=PRES	bar

Edit selected variable

Manipulated variable
Variable: 1
Type: Stream-Var
Stream: 17
Substream: MIXED
Variable: PRES
Units: bar

Manipulated variable limits
● Equidistant ○ Logarithmic ○ List of values
Start point: 21 bar
End point: 40 bar
○ Number of points: 20
● Increment: 1 bar

Figure 7.7 Sensitivity analysis dependent variable

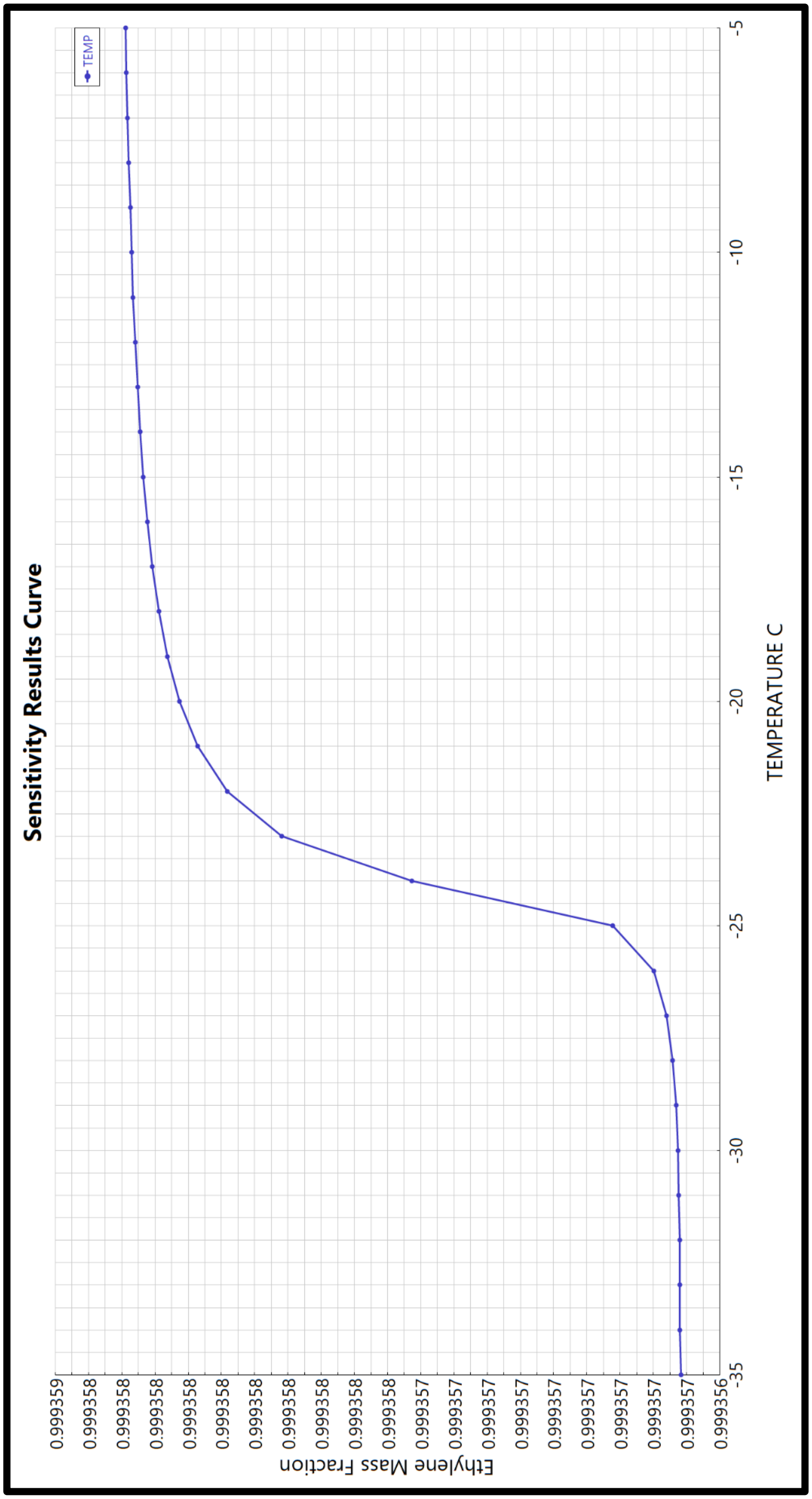


Figure 7.8 Temperature Sensitivity analysis

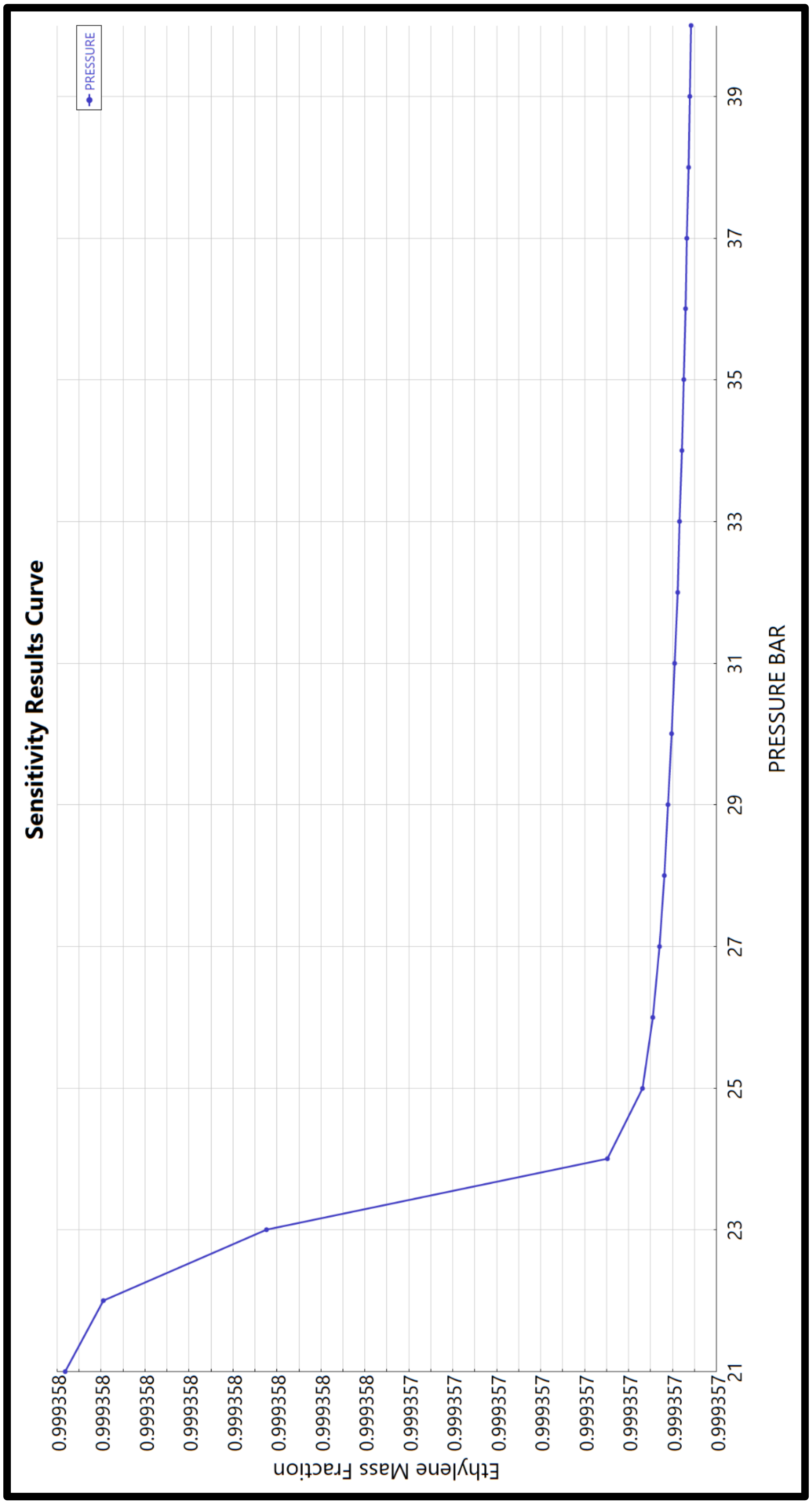
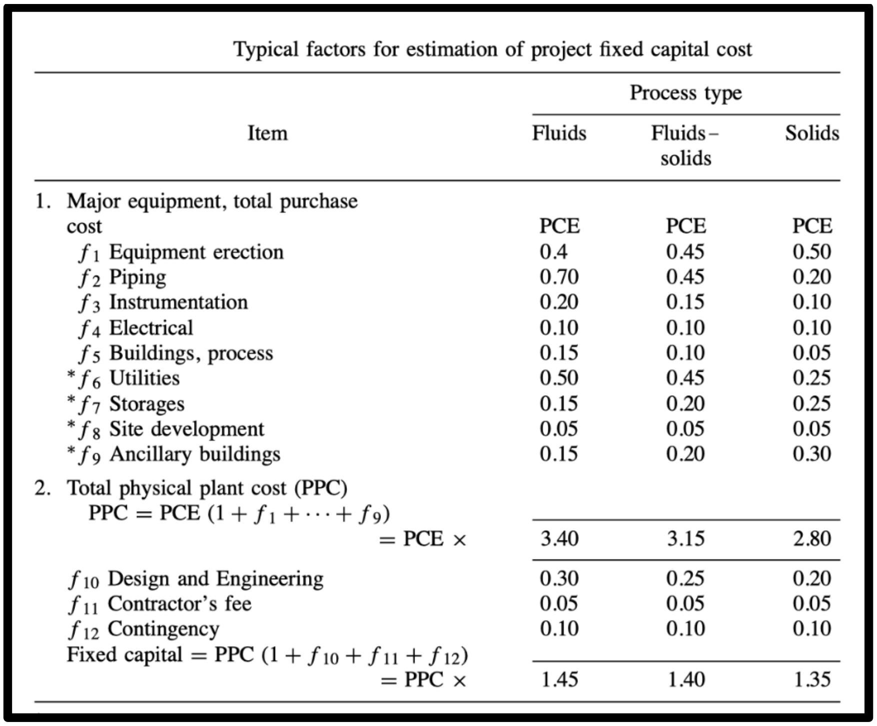


Figure 7.9 Pressure sensitivity analysis

8 Costing and Economic Analysis

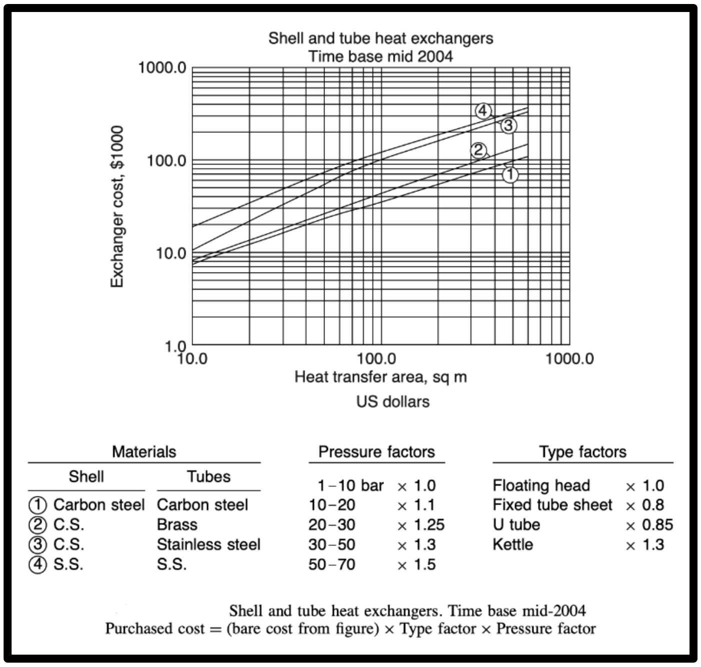
The costing of our plant was done both manually and through Aspen Plus. The following data was used to estimate the cost of total plant.



Typical factors for estimation of project fixed capital cost

	Process type		
Item	Fluids	Fluids–solids	Solids
1. Major equipment, total purchase cost	PCE	PCE	PCE
f_1 Equipment erection	0.4	0.45	0.50
f_2 Piping	0.70	0.45	0.20
f_3 Instrumentation	0.20	0.15	0.10
f_4 Electrical	0.10	0.10	0.10
f_5 Buildings, process	0.15	0.10	0.05
$^*f_6$ Utilities	0.50	0.45	0.25
$^*f_7$ Storages	0.15	0.20	0.25
$^*f_8$ Site development	0.05	0.05	0.05
$^*f_9$ Ancillary buildings	0.15	0.20	0.30
2. Total physical plant cost (PPC)			
PPC = PCE $(1 + f_1 + \cdots + f_9)$			
= PCE ×	3.40	3.15	2.80
f_{10} Design and Engineering	0.30	0.25	0.20
f_{11} Contractor's fee	0.05	0.05	0.05
f_{12} Contingency	0.10	0.10	0.10
Fixed capital = PPC $(1 + f_{10} + f_{11} + f_{12})$			
= PPC ×	1.45	1.40	1.35

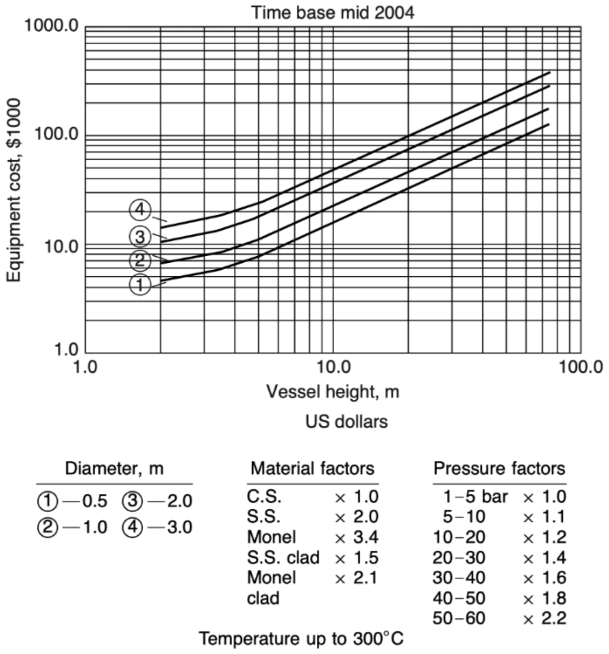
Figure 8.1 Factors for estimation of fixed capital cost



Materials		Pressure factors		Type factors	
Shell	Tubes				
① Carbon steel	Carbon steel	1–10 bar	× 1.0	Floating head	× 1.0
② C.S.	Brass	10–20	× 1.1	Fixed tube sheet	× 0.8
③ C.S.	Stainless steel	20–30	× 1.25	U tube	× 0.85
④ S.S.	S.S.	30–50	× 1.3	Kettle	× 1.3
		50–70	× 1.5		

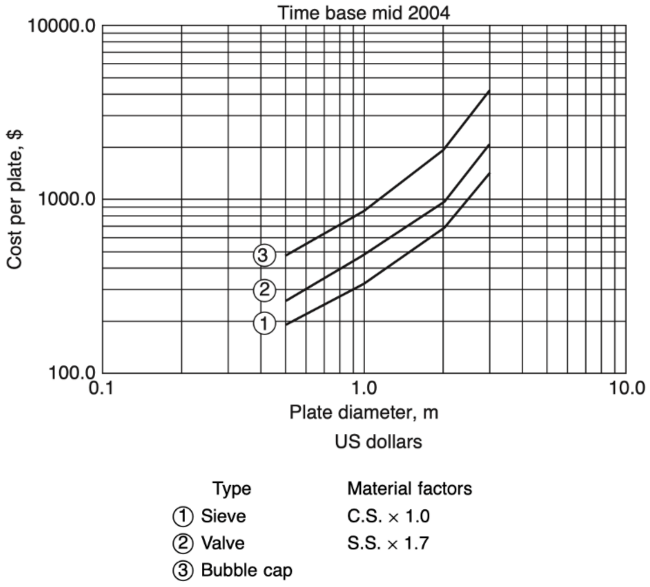
Shell and tube heat exchangers. Time base mid-2004
Purchased cost = (bare cost from figure) × Type factor × Pressure factor

Figure 8.2 PCE for Shell and Tube HE



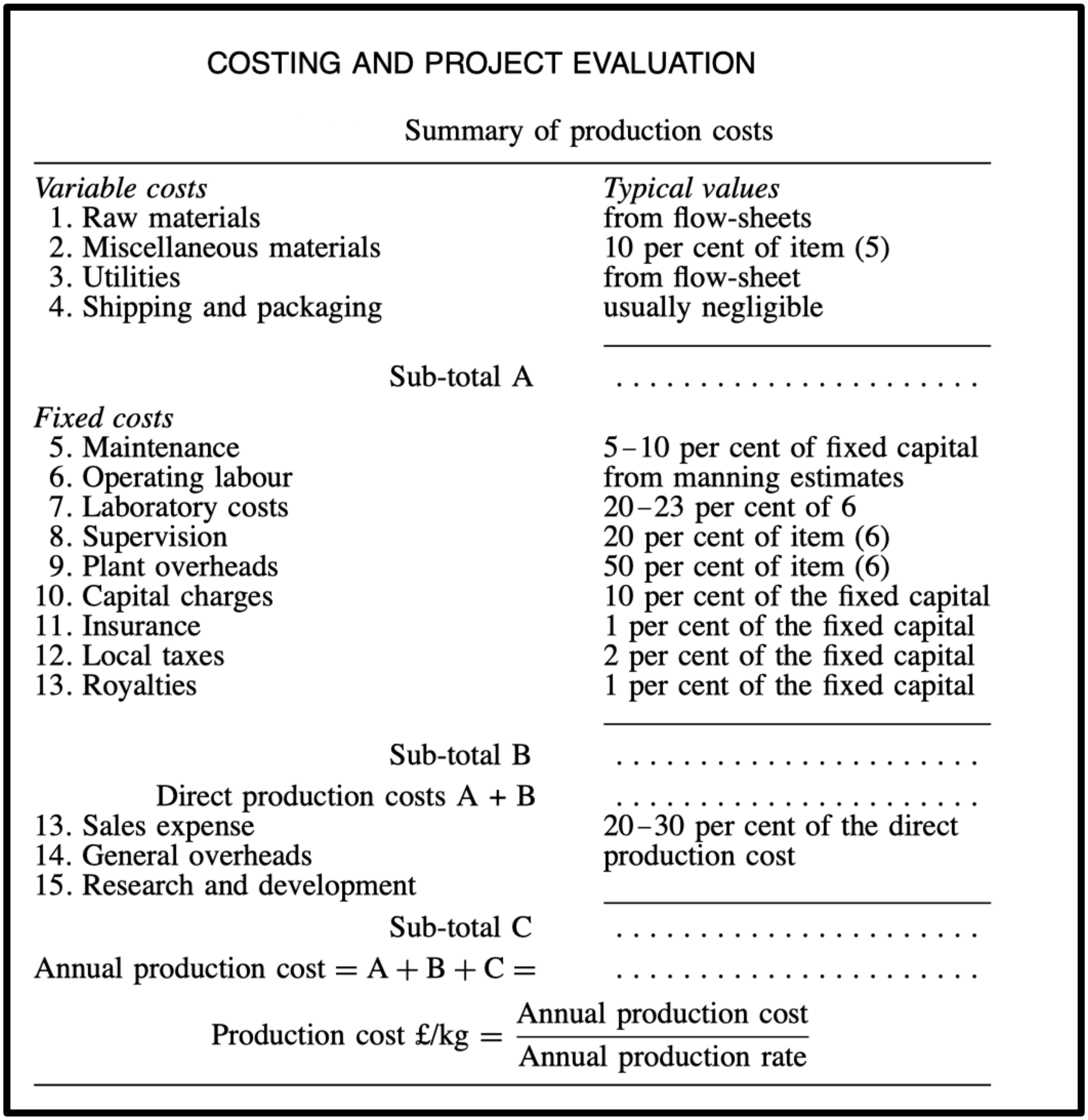
Vertical pressure vessels. Time base mid-2004.
Purchased cost = (bare cost from figure) × Material factor × Pressure factor

Figure 8.3 PCE for Vessels



Column plates. Time base mid-2004
Installed cost = (cost from figure) × Material factor

Figure 8.4 PCE for Plates



COSTING AND PROJECT EVALUATION

Summary of production costs

Variable costs	*Typical values*
1. Raw materials	from flow-sheets
2. Miscellaneous materials	10 per cent of item (5)
3. Utilities	from flow-sheet
4. Shipping and packaging	usually negligible
Sub-total A	. . . .
Fixed costs	
5. Maintenance	5–10 per cent of fixed capital
6. Operating labour	from manning estimates
7. Laboratory costs	20–23 per cent of 6
8. Supervision	20 per cent of item (6)
9. Plant overheads	50 per cent of item (6)
10. Capital charges	10 per cent of the fixed capital
11. Insurance	1 per cent of the fixed capital
12. Local taxes	2 per cent of the fixed capital
13. Royalties	1 per cent of the fixed capital
Sub-total B	. . . .
Direct production costs A + B	. . . .
13. Sales expense	20–30 per cent of the direct production cost
14. General overheads	
15. Research and development	
Sub-total C	. . . .
Annual production cost = A + B + C =	. . . .

$$\text{Production cost £/kg} = \frac{\text{Annual production cost}}{\text{Annual production rate}}$$

Figure 8.5 Summary of production costs

The following table shows all the individual and then combined values of our plant equipments.

Table 24 Total production cost of our project

COSTING AND PROJECT EVALUATION			
		Summary of production costs	
	Variable costs	Typical values	Costs ($)
1	Raw materials.	from flow-sheets	8451204
2	Miscellaneous operating materials.	10 per cent of item (5)	81035
3	Utilities (Services).	from flow-sheet	796689
4	Shipping and packaging.	usually negligible	0
	Sub-total A		**9328928**
	Fixed costs		
5	Maintenance (labour and materials).	5 -10 per cent of fixed capital	810352
6	Operating labour.	from manning estimates	1000000
7	Laboratory costs.	20 23 per cent of 6	200000
8	Supervision	20 per cent of item (6)	200000
9	Plant overheads	50 per cent of item (6)	500000
10	Capital charges.	10 per cent of the fixed capital	1543529
11	Rates (and any other local taxes).	1 per cent of the fixed capital	154353
12	Insurance.	2 per cent of the fixed capital	308706
13	License fees and royalty payments.	1 per cent of the fixed capital	154353
	Sub-total B		4871292
	Direct production costs A + B		**14200220**
14	Sales expense	20 -30 per cent of the direct production cost	2840044
15	General overheads		0
16	Research and development		0
	Sub-total C		2840044
	Annual production cost + A + B + C =		**17040264**
	Production cost $/kg =	$\frac{\boldsymbol{Annual\ production\ cost}}{\boldsymbol{Annual\ production\ rate}}$	0.76

Table 25 Equipment costs of our project

Name	**Equipment Cost (2004) [USD]**	**Equipment Cost (2019) [USD]**
HE-03	6960	11120
HE-07	5383	8600
Compressor-03	506151	808700
HE-02	12869	20562
Compressor-02	487375	778700
HE-01	7941	12688
Separators	9764	15600
Distillation-condenser	23471	37500
Distillation-reflux drum	11391	18200
Distillation-reboiler	9826	15700
Distillation-reflux pump	3630	5800
Distillation-tower	82116	131200
HE-06	5445	8700
Pump-01	2942	4700
HE-05	5508	8800
Reactor	752119	1201694
HE-04	14977	23929
Compressor-01	466971	746100
HE-08	6384	10200
Total	**2421223**	**3868493**

8.1 Cost Estimation

The following equations were used to find out the production cost and the payout period of our plant.

$$Cost\ in\ year\ 2019 = Cost\ in\ year\ 2004 \times \frac{CPE\ Index\ in\ year\ 2019}{CPE\ Index\ in\ Year\ 2004}$$

CPE Index 2019 = 641.10

CPE Index 2004 = 401.51

$$Production\ Cost\ \left(\frac{USD}{kg}\right) = \frac{Annual\ Production\ Cost}{Annual\ Production\ Rate}$$

$$Payout\ Period = \frac{Total\ Fixed\ Investment}{After - Tax\ Cash\ Flow}$$

$$\text{Total Physical Plant Cost} = 11{,}025243 \text{ USD}$$

$$\text{Fixed Capital} = 15{,}435285 \text{ USD}$$

$$Working\ Capital = 771746\ USD$$

$$\text{Total Investment Required} = 16{,}207050 \text{ USD}$$

$$\text{Production Cost} = 15{,}907803 \text{ USD}$$

$$\text{Net Income} = 20{,}403600 \text{ USD}$$

$$\text{Payout Period} = 4.59 \text{ years}$$

A pay out period of 4.6 years shows that the designed plant is highly feasible in both economic and efficiency terms.

9 Instrumentation

Controllers were installed on the following streams and equipments:

Table 26 Controllers installed in the plant

Equipment	Name of Controller	Type of Controller	Manipulated Variable	Controlled Variable
Ethanol Tank	LC	PI	Flowrate	Ethanol Level
Heat Exchanger 2	TC	PI	Steam Flowrate	Temperature
	FC	PI	Valve opening	Steam Flowrate
Reactor	TC	PI	Steam Flowrate	Reactor Temperature
	FC	PI	Valve opening	Product Flowrate
Separators	LC	PI	Flowrate	Product Level
Distillation Column	TC	PI	Flowrate of Refrigerant	Temperature of inlet
	PC	PI	Flowrate	Pressure
	LC	PI	Flowrate of Inlet	Level
	FC	PI	Valve opening	Inlet Flowrate
	FC	PI	Valve opening	Reflux Flowrate
	TC	PI	Refrigerant Flowrate	Reflux Temperature
	FC	PI	Valve opening	Reboiler Outlet Flowrate
	TC	PI	Steam Flowrate	Reboiler Outlet Temperature

10 HAZOP

The HAZOP study was employed on the whole process in two major loops, with the first one being the reaction train, including pumps, pre and super-heaters and the reactor. While for the separation loop consisting of knock out drum, distillation column, heat exchangers and compressors the procedure was carried out separately. Table 1 addresses the issues encounterable in the reaction loop, followed by the second table which is concerned with the separation equipments.

Table 27 HAZOP Analysis for reaction loop

Guide Word	Deviation	Causes	Consequences	Action Required
None	No flow	Pump Fails, Line Fracture, LCV fails	Loss of Feed to reactor	Install kickback on pump, institute regular patrolling and inspection of transfer lines
More of	More Temperature	High storage tank temperature, Higher flow of steam (flow controller fails)	Lower product (ethylene) selectivity,	Install temperature sensor at storage tank,
	More Pressure	LCV closes, with pump running	Lower product yield, line fracture	Install a Pressure Gauge upstream of LCV
	More Flow	LCV fails open or LCV bypass open in error	low conversion in reactor	Install a relief valve
Less of	Less flow	Leakage, possible line damage,	Production loss	Regular patrolling and inspection of transfer line
	Less Temperature	Winter conditions, lower steam flow	Drain line freeze up	Install TC on storage tank, FC on steam stream.

Table 28 HAZOP Analysis for separation loop

Guide Word	Deviation	Causes	Consequences	Action Required
None	No flow	Line Fracture	Loss of product to be purified	Institute regular patrolling and inspection of transfer lines
More of	More Temperature	Lower cooling water flow,	Low separation efficiency	Install temperature sensors to govern cooling water and refrigerant flow,
	More Pressure	LCV closes, with pump running	Lower product yield	Install a PG and a throttling valve
	More Flow	LCV fails open or LCV bypass open in error	Low efficiency for separation equipment specially separators	Install a flow controller which regulates a valve opening, install a relief valve
Less of	Less flow	Leakage, possible line damage,	Production loss	Regular patrolling an inspection of transfer line
Other	Equipment Failure	water in compressor/ cryogenic feed damages impeller vanes and trays	Poor separation and compression	Install a drain at the bottom of the compressor to collect water. Manage separator parameters carefully.

11 Conclusions

The first loop (reaction train) was operated at a low pressure since, it aided ethylene selectivity, while the second loop (separation) was operated on a high pressure to obtain high efficiency of the separation equipment. The process has been optimized in terms of production, cost and energy efficiency, while removing the environmental hazards at the same time.

- Through the use of Nano-CAT the conversion of ethanol and selectivity of ethene were increased to 99.2 and 98.69 percent respectively, thereby making the process cost effective (through less separation equipment and utility cost).

- The product distribution with the utilized catalyst was such that, no CO_2 was produced while the amount of CO produced was very low, thus removing need for any absorber (for CO_2 removal) and C_2 stripper (for CO removal in the last step) to obtain polymer grade purity.

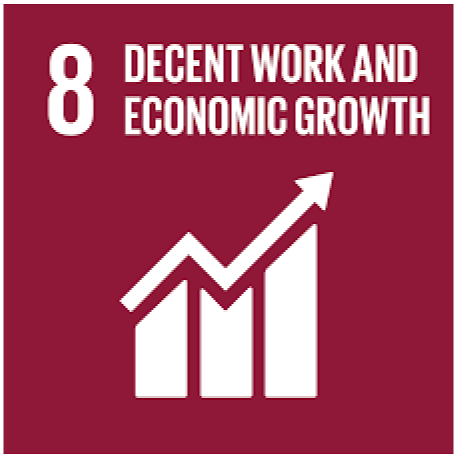
- Very low amount of CO in the product and no CO_2 also meant that the process was extremely environment friendly, and was almost along the lines of being a green process. High catalyst passivity ensured that frequent regeneration (with de-coking being a phenomenon releasing CO_2) also validated the green process claim.

- Through Implementation of this process, a sustainable pathway was mapped out, since ethanol being a renewable raw material is easily available in a country like Pakistan, with the Sub-continental nation being its 6th largest exporter.

- The process was made energy efficient first through reducing the reaction temperature, while integrating the network of exchangers, so as to use minimum energy.

- The project was able to propose a way for curbing the ethylene demand in the nation which could give a big boom to the economy.

The project was able to meet 4 sustainability goals, which were climate action, economic growth, responsible production and consumption and industry innovation and infrastructure development.


8
DECENT WORK AND ECONOMIC GROWTH


9
INDUSTRY, INNOVATION AND INFRASTRUCTURE


12
RESPONSIBLE CONSUMPTION AND PRODUCTION


13
CLIMATE ACTION

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