THE FIRST STEP FOR SUCCESS

STUDENT'S BOOK OF PETROCHEMICAL TECHNOLOGY

VOLUME 2



ROSNI YUSOFF
NOR HATINI BAHARIN
SHARIFFAH NUR JANNAH SYED ZAINOL ABIDIN

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Published in Malaysia by:
Politeknik Tun Syed Nasir Syed Ismail
Hab Pendidikan Tinggi Pagoh
KM 1 Jalan Panchor 84600 Pagoh, Johor.

to a new student who is keen to make money through oil and gas

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	Page
Separation Processes	3
1.1 Type of Main Separations and Construction Designs	4
1.1.1 Distillation	4
1.1.2 Absorption 1.1.3 Adsorption	10 14
1.1.4 Liquid-liquid Extraction 1.2 Differences Between Type of	18
Separation Processes	20
Activity 1.0 Review Questions	22
Basic Plant Operations	23
2.1 Gas Processing Plant	24
2.1.1 Natural Gas Flow Process 2.1.2 Function of Equipment in Gas	26
Processing Plant 2.1.3 Dew Point Control Unit (DPCU)	28
2.1.3 Dew Point Control Onit (DPCO) 2.1.4 Product Recovery Unit (PRU)	30 33
2.1.5 Unit Liquefied Petroleum Gas (LPG) 35
2.1.6 Acid Gas Removal Unit (AGRU) 2.1.7 Glycol Regeneration Unit (GRU)	37 38
2.1.7 Glycol Regeneration Onit (GRO) 2.1.8 Product of Gas Processing Plant	39
2.2 Oil Refinery Plant	39
2.2.1 Flow Process of Oil Refinery Plant	45
2.2.2 Function of Equipment in Oil Refine Plant	y 47
2.2.3 Refining Product and Their Usage	50
Activity 2.0 Review Questions	53
Petrochemical Plants	54
3.1 MTBE and Polypropylene Plant	57
3.2 Ethylene and Polyethylene Plant	63 69
3.3 Ammonia and Urea plant 3.4 Methanol Plant	77

3.5 Liquefied Natural Gas Plant3.6 Acrylic Acid Plant Activity 3.0 Review Questions

Glossary

Distillation _Process Method of separating mixtures based on differences in their boiling points.

Absorption Process _Method removal of one or more selected components from a mixture of gases

Adsorption Process _Mass transfer process or a molecule gas or liquid (adsorbate) that forms a bond to the surface (adsorbent)

Extraction _Method to separate one or more of the components in the mixture from one phase into the other by using a solvent.

Cracking _The process of splitting a large heavy hydrocarbon molecule into smaller, lighter components. The process involves very high temperature and pressure and can involve a chemical catalyst to improve the process efficiency.

Coke _An insoluble organic deposit that has low hydrogen content. Coke, also known as pyrobitumen, is formed by thermal cracking and distillation during in-situ combustion.

Knock out Liquid condensed by a scrubber following a compression and cooling process.

Liquefied petroleum gas _Gas mainly composed of propane and butane, which has been liquefied at low temperatures and moderate pressures. The gas is obtainable from refinery gases or after the cracking process of crude oil.

Isomerization _The process in which a molecule, ion or molecular fragment is transformed into an isomer with a different chemical structure.

Polymerization _A process in which monomers combine chemically to produce a very large chainlike or network molecule called a polymer.

Demethanizer _The unit that separates methane rich residue gas from the heavier hydrocarbon in the feed natural gas stream.

Desulphurization A chemical process for the removal of sulphur from a material.

Synthesis gas (syngas) A gaseous mixture mostly of H₂ and CO.

Methanation _Conversion of carbon monoxide and carbon dioxide to methane through hydrogenation.



Preface

This e-book is illustrated based on the course structure of the Diploma in Mechanical (Petrochemical) Engineering Program. This e-book is a continuation of the **Student's Book of Petrochemical Technology**, **Volume 1.** After crude oil and gas exploration, the processes related to these feedstocks are revealed. Process flows and equipment functions as well as product applications are discussed in detail. This e-book would help students to understand well in the petrochemical industry. On top of that, this e-book would give a smooth foundation for the student who wishes to make money through this career!

Rosni Yusoff Nor Hatini Baharin Shariffah Nur Jannah Syed Zainol Abidin 2021

Separation Processes

1.0 Separation Processes

Basic processes of separation

Hydrocarbon streams as produced at the wellhead are composed of a mixture of gas, liquid hydrocarbons, and sometimes free water. In most cases it is desirable to separate these phases as soon as possible after bringing them to the surface and handle or transport the two or three phases separately. This separation of the liquids from the gas phase is accomplished by passing the well stream through an oil-gas or oil-gas water separator. Distillation process is the top of the separation process before undergoing the refining process.

1.1 Type of Main Separations and Construction Designs

In general, separation processes may use physical, chemical, or electrical forces typed to isolate or concentrate selected constituents of mixture. These design techniques are very essential in petroleum refining, chemical and materials processing industries. Distillation, extraction, and absorption as well as adsorption are widely used in simple separation design in petrochemical industries.

1.1.1 Distillation

Distillation is a method of separating mixtures based on differences in their boiling points. Distillation is a unit operation, or a physical separation process, and not a chemical reaction. Figure 1.1 shows the tower of distillation plants and its separation components.

Heat is supplied to heat up the mixture of components to the boiling point before the separation process occurs. The component with a lower boiling point will change to vapor and leaves from the top of the distillation column. The component with a higher boiling point will produce from the bottom of the column.

Volume 2 Petrochemical Technology



Figure 1.1 The Fractional Distillation Column and Its Separation Component

To understand more about distillation, we must know the terms used:

- **Feed** mixture of two or more components of chemicals
- Overhead product portion of the charge which leaves the top of the distillation column as a vapour
- Bottom product portion of the charge at the bottom of the distillation column as a liquid
- Reflux In distillation, the return of part of the condensed vapor to the fractionating column to assist in making a more complete separation of the desired fractions. The material returned is reflux.
- Reboiler An auxiliary unit of a fractionating tower designed to supply additional heat
 (to generate vapors) at lower portion of the tower
- Condenser heat exchanger that condense overhead product in vapour to liquid through a cooling medium.
- Reflux Accumulator Vessel with high pressure. Accumulate overhead product before recycling as a reflux (Reintroduce to column) or as overhead product

Construction Design

Figure 1.2 shows the distillation column (fractionator) and the support equipment which act as an important component during distillation operation.

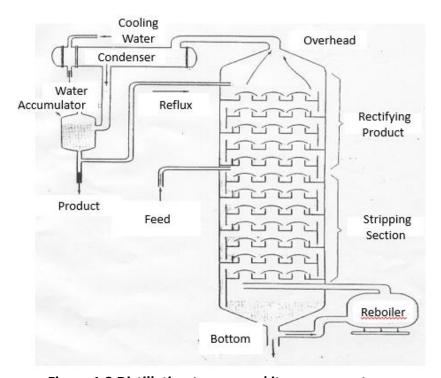


Figure 1.2 Distillation towers and its component

Vessel

Industrial distillation is typically performed in large, vertical cylindrical columns known as distillation towers or distillation columns with diameters ranging from about 65 cm to 16 m and heights ranging from about 6 m to 90 m or more.

Material: Stainless steel - to avoid corrosion

Equipment: Trays & Packing

- Distillation equipment includes two major categories:
 - i- Trays
 - ii- Packing

I. Tray

Trays force a rising vapor to bubble through a pool of descending liquid.

- Types of tray: bubble cap tray & valve tray
- Material: Steel Trays are welded to the vessel
- Trays are fitted with a device called bubble caps (see Figure 1.3 and 1.4).

The purpose of a bubble cap is to force the vapour coming up through the trays to bubble through the liquid standing several inches deep on that tray.

This bubbling is the essence of distilling operation: the hot vapour (starting out at 750°F) bubbles through liquid.

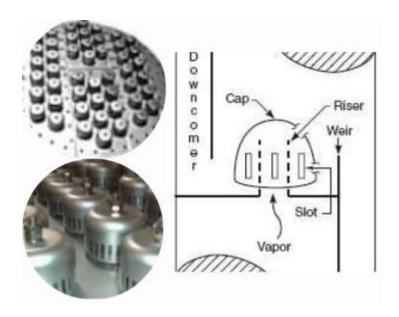


Figure 1.3 Bubble Cap Trays

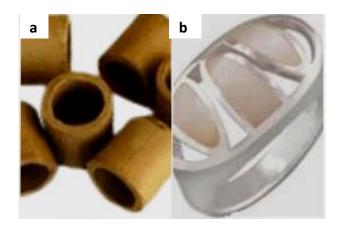


Figure 1.4 Example of Bubble Cap Tray of a) Rashing Ringe and b) Slotted Ringe

II. Packing

Packing creates a surface for liquid to spread on. The thin liquid film has a high surface area for mass-transfer between the liquid and vapor. Packing can be used to substitute trays in a small column. Material made of plastic, metal or ceramic. The use of packing depends on the gas or liquid in the column. Figure 1.5 shows an example of a packed column used in industry.

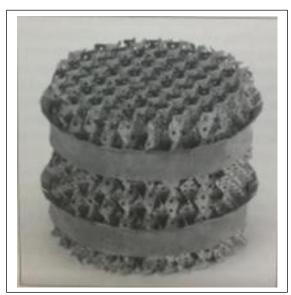


Figure 1.5 Packed Column

Volume 2 Petrochemical Technology

Types of Distillation

The two major types of distillation are:

- a. Continuous distillation Continuously takes a feed and separates it into two or more products.
- b. Batch distillation takes on lot (or batch) at a time of feed and splits it into products by selectively removing the more volatile fractions over time

Distillation Process Flow

- 1. Feed mixture of two or more components usually in liquid phase e.g. crude oil.
- 2. Feed is separated into one distillate fraction and one bottoms fraction through a heater.
- 3. The "lightest" products (those with the lowest boiling point) exit from the top of the column.
- 4. From the top of the column, then the vapour enters into condenser reflux. Here, vapour changes to liquid.
- 5. The flow of liquid enters to reflux or column as a reflux. The flow level is controlled by a controller.
- 6. The products from the overhead must have a high purity before being sent to the storage tank.
- 7. The "heaviest" products (those with the highest boiling point) exit from the bottom of the column and are often called the bottoms.
- 8. The products are in liquid. From the bottom of the column, they enter into the reboiler where some of the products change to vapour and send back to the bottom of the column.
- 9. To assure the heaviest don't get out the top of the column, sometimes some of the vapor will run through a cooler. Whatever is condensed is reintroduced to a lower tray. Whatever is still vapour is sent off as a product. The process is a form of refluxing.

Application of Distillation

The application of distillation can roughly be divided in four groups:

- a) Laboratory scale
- b) Industrial distillation (petroleum refining, chemical processing, petrochemicals, and natural gas processing)
- c) Distillation of herbs for perfumery and medicinal (herbal distillate)
- d) Food processing (beverages)

Most of the distillation process involved the components in liquid form. What if the components that are being separated are in gas form? E.g. O_2 gas and N_2 gas in air. Can we use a distillation method?

Yes, perhaps, but the process needs a very high pressure to form a liquid phase. So as an alternative, an absorption process takes place.

1.1.2 Absorption



Figure 1.6 A simple Illustration of sponge absorb water

Absorption is a mass transfer process or a change of substance from gas phase to liquid phase or the removal of one or more selected components from a mixture of gases is called absorption. In simple situations, the absorption process can be seen during the absorption of water by sponge (Figure 1.6).

Absorption process is used to separate a soluble gas in the solution that is being used from the original gas mixture. To understand more about absorption, we must know the terms used:

- Solute the component that is being removed or absorbed.
- Solvent the solution that can dissolve solute.
- Rich solvent the solvent that contained solute.
- Lean solvent the solution that contained no solute.
- Absorber an equipment used in the absorption process.

Gas -Liquid Absorption

Example of a liquid gas system is an absorption process where a soluble gas is scrubbed from a mixture of gases by means of a liquid. Figure 1.7 shows a simple gas and liquid in and out from the column.

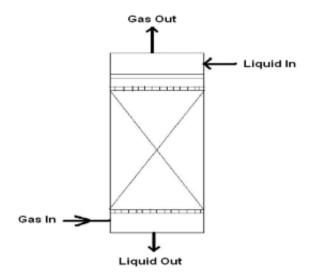


Figure 1.7 A Simple Illustration of Gas and Liquid in and out from Column for Absorption Process

Construction Design

Figure 1.8 shows the construction design of Absorption Column (Absorber). Typically, the sections include as follows:

- Cylindrical column with a gas inlet and distributing space at the bottom.
- A liquid inlet and distributor at the top.
- Gas and liquid outlets at the top and bottom respectively.
- Column packing to ensure intimate contact between the liquid and the gas.
- Packing support to give strength.
- The *shell of the column* may be constructed from metals, ceramics, glass or plastics material or from metals with a corrosion-resistant lining.
- The *column* should be mounted truly vertically to help uniform liquid distribution.
- The *bed of packing* rests on a support plate which should be designed to have at least 75% free area for the passage of the gas to offer as slow resistance as possible.

Process Flow of Absorption Process

- The rich solvent is regenerated in the stripper column (regeneration process) after a gas-liquid absorption process is completed.
- The solute containing gas or solute-rich gas enters the bottom of the absorber (Figure 1.8).
- Lean solvent is recycled from the stripper and enters the top of the absorber.
- In absorber, lean solvent flows downward through the spaces in the packing and absorbs the solute from the gas.
- Treated gas or gas without solute leaves the top of the absorber.
- The solution which contains solute or rich solvent leaves the bottom of absorber and enters the stripper column for the regeneration process.
- Distillation method is used in the regeneration process.

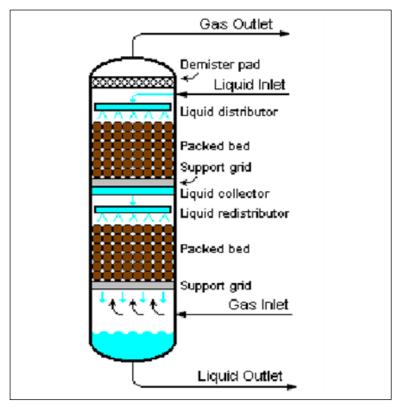


Figure 1.8 Construction Design of Absorption Column

The principles of increasing rate of absorption

The principle rate of absorption can be further explained based on Figure 1.9

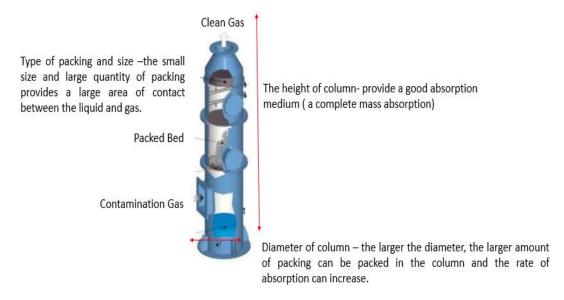


Figure 1.9 The Principle Rate of Adsorption Take Places in Column.

Volume 2 Petrochemical Technology

Application of Absorption

Table 1.1 Application of Absorption in Refinery Process

Process Name	Action	Purpose	Feedstock	Product
Amine Treating	Treatment	Remove acid contamination	Sour Gas, Hydrocarbon with CO2 and H2S	Acid-free gases
Drying and sweetening	Treatment	Remove H2O and sulphur compound	Liquid hydrocarbon, LPG, alkylated feedstock	Sweet and dry hydrocarbons
Desalting (Pre- treatment)	Treatment	Remove contaminants	Crude oil	Desalted crude oil

1.1.3 Adsorption



Figure 1.10 Person Wearing a Gas Mask

Adsorption is a mass transfer process or a molecule gas or liquid (adsorbate) that forms a bond to the surface (adsorbent). For example, activated charcoal (carbon) in a gas mask (Figure 1.10) attracts toxic gas molecules, allowing the person wearing the mask to breathe fresh air.

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To understand more about adsorption, we must know the terms used:

- Adsorbate material being adsorbed
- Adsorbent material doing the adsorbing. (e.g., activated carbon or ion exchange resin)
- Adsorber an adsorption column consisting of adsorbents

Characteristic of Adsorption

Physical Adsorption

- Physical adsorption Van der Waals attraction between adsorbate and adsorbent.
- The attraction is not fixed to a specific site and the adsorbate is relatively free to move on the surface.
- This is relatively weak, reversible, adsorption capable of multilayer adsorption.

Chemical Adsorption

- Chemical adsorption some degree of chemical bonding between adsorbate and adsorbent characterized by strong attractiveness.
- Adsorbed molecules are not free to move on the surface.
- There is a high degree of specificity ad typically a monolayer is formed.
- The process is seldom reversible.

Exchange Adsorption

- Exchange adsorption (ion exchange) electrostatic due to charged sites on the surface.
- Adsorption goes up as ionic charge goes up and as hydrated radius goes down.

Construction Design

i. An adsorber column consists of adsorbent in large quantity.

- Petrochemical Technology
- ii. The regeneration process is required to repeat adsorbate removal that is adsorbed to the adsorbent surface.
- iii. Three adsorber columns are required to ensure the separation process can be done continuously.
- iv. Adsorbent consists of natural or synthetic materials. Most of the adsorbent surface area is interior in micro- and macropores.
- v. The common type of adsorbents used: Activated Carbon, Activated Alumina, Silica Gel, Fuller's Earth, and Molecular Sieve.

Table 1.2 Surface Area of Adsorbent

Pore size	% pore volume	% surface area
Micro	30 – 60	<95
Meso	< 10	<5
macro	25 - 30	negligible

Adsorption Process Description

- a) Gas feed consist a mixture of Gas A and Gas B (Figure 1.11)
- b) Gas A (adsorbate) is adsorbed to the adsorbent surface.

Phase 1

- a) Feed (Gas A and Gas b) enters to the bottom of adsorber at the lower temperature.
- b) The selected adsorbent allows Gas A to be adsorbent and releases Gas B, thus, gas B leaves the adsorber.
- c) After a period, the adsorbent reaches its saturation which time all pores are filled with gas A.
- d) The adsorption process and feed inlet must be stopped after the process.
- e) Now, gas A must be removed from the adsorbent surface. Refer to phase 2.

Phase 2

- a) Adsorption process is proportional inverting to the temperature.
- b) Adsorbent tends to release the adsorbed components (Gas A) when the temperature increased.
- c) Therefore, the hot gas which is also as a feed flows to the top of adsorber to release as A from adsorbent.

Phase 3

- a) The third phase is required to cool down the adsorption column.
- b) The purpose of this stage is to provide a lower temperature of the adsorption column so that the adsorption process can be done continuously.

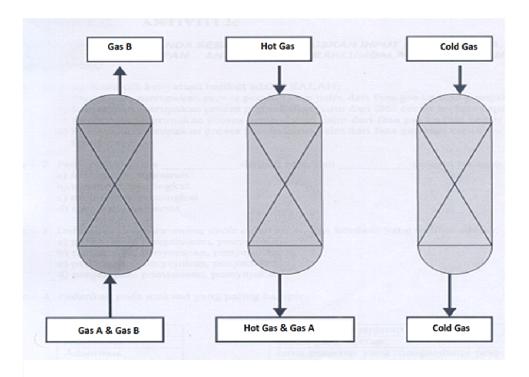


Figure 1.11 Process Flow Diagram of Gas Adsorption

Petrochemical Technology

1.1.4 Liquid-liquid Extraction

Extraction is an alternative if the cost of distillation is too expensive or not practical. The two-phase pair can be gas-liquid, vapor-liquid and liquid-liquid or fluid-solid extraction. In this chapter, liquid-liquid extraction separation processes are considered.

- **2** Extraction uses two immiscible phases to separate one or more of the components in the mixture from one phase into the other by using a solvent.
- **2** Example, boiling tea leaves in water extracts the tannins and caffeine out of the leaves and into the water.

Liquid-liquid extraction is also known as extraction with solvent, is a method to separate the components of a mixture of liquids by means of a solvent in which the component or the components that are to be extracted have marked solubility in respect to the others.

Extraction may be used to separate more than two components; and mixture of solvents, instead of single solvents, are needed in some applications.

For example, an organic MTBE solution is extracted with aqueous sodium bicarbonate solution. This base removes benzoic acid as benzoate but leaves non-acidic benzil (yellow) behind in the upper organic phase.

Liquid-liquid Extraction Application

- Nuclear reprocessing
- Production of fine organic compounds
- Processing of perfumes

To understand more about liquid-liquid extraction, we must know the terms used:

- 1. **Feed** The liquid inlet contained with solute to be separated.
- 2. **Extraction solvent** is a liquid that dissolves a solute from feed, resulting in a solution.

- 3. **Solute** the component in liquid phase to be extracted.
- 3. **Extract** solute from feed that is dissolved by extraction solvent.
- 4. **Raffinate** the liquid inlet in which the solute is separated.

Extraction Process Description

- The solute in the feed (acetic acid+H2O) is separated by attracting it with extraction solvent (ethyl acetate). Therefore, the solute can be dissolved in an extraction solvent (Figure 1.12).
- 2. Then the solute (acetic acid) is separated from the liquid inlet. Therefore, the liquid inlet which has no solute leaves from the top of the extraction column as a raffinate (water).
- 3. Extract in extraction solvent and solute leaves from the bottom of the extraction column.

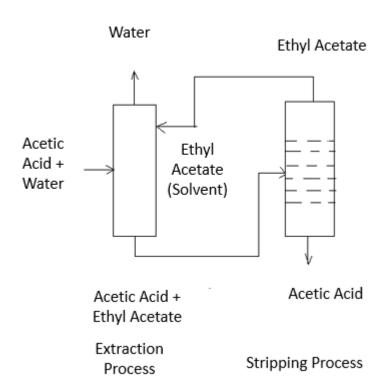


Figure 1.12 Process Flow Diagram of Liquid-liquid Extraction

Volume 2 Petrochemical Technology

1.2 Differences Between Types of Separation Process

a) Difference between distillation and extraction

Table 1.3 Differences Between Distillation and Extraction Process

DISTILLATION VS EXTRACTION		
Distillation		Extraction
Process	Distillation is a process of separation (Purifying) liquid by a process of heating and cooling	Extraction is a process of extraction unwanted/wanted liquid or solid using solvent/absorbent
Method separation	Use difference boiling point of chemical component in a mixture	Use difference solubility
Degree of separation	Relative volatility as a degree of separation	Relative solubility as a degree of separation
Phase involve	For mixture of liquid phase only	For mixture/substance in liquid and solid phase

b) Differences between absorption and adsorption

Table 1.4 Differences Between Distillation and Extraction Process

ABSORPTION VS ADSORPTION			
	Absorption	Adsorption	
Process	Phase 1 Phase 2	Phase 1 Phase 2	
	Assimilation of molecular species throughout the bulk of the solid or liquid	Process of adhesion of molecules of liquid or gases onto the surface of a solid particle.	
	Bulk Phenomena	Surface Phenomena	
Heat Exchange	Endothermic	Exothermic	

Activity 1.0 Review Questions

- 1. Define
 - a) Distillation
 - b) Absorption
 - c) Adsorption
 - d) Extraction (Liquid-liquid)
- 2. List and explain the important components in distillation equipment.
- 3. Explain the principles in order to increase the rate of reaction during the absorption process.
- 4. List 3 (three) example application of adsorption in refinery process
- 5. Sketch and label the basic distillation and extraction process

Basic Plant Operations

2.0 Basic Plant Operations

Development of the petroleum industry is now very favorable around the world. Furthermore, development in our country (Malaysia) depends on petroleum production. Petroleum industry operations in Malaysia is dominated by Petronas Sdn. Ltd. as well as other companies such as Shell Co. Sdn. Ltd. Esso and others.

Petroleum industry was once focused on oil production, but now has changed to its current gas production. This is due to declining oil reserves. Moreover, it is difficult to find new oil fields and potential for development. So now, the petroleum industry is more focused on gas production technology as well as to find other alternatives to continue oil production.

In Industrial petroleum operations, there are two plants that are designed to process oil and gas as well as plants - other petrochemical plants. For oil processing, oil refineries were designed and for processing gas, a gas processing plant was made. So in this unit, we will discuss gas processing plants and oil refineries, particularly in Malaysia.

2.1 Gas Processing Plant

Development of the gas industry in Malaysia started with the finding of gas wells in Sarawak, Sabah and Terengganu in early 1970. Following the finding of gas, a few studies have been conducted to enable the use of found gas to be commercialized. Strategies have been designed so that the gas can be used as a substitute for petroleum products.

To maximize the use of Malaysia's gas reserves that are quite a lot, the production gas from gas fields in Sabah and Sarawak have been identified for export. While production gas from gas fields in Terengganu were processed for domestic use.

Volume 2 Petrochemical Technology

Gas in gas fields at Sarawak has been sent to the MLNG plant (Malaysian Liquefied Natural Gas) plant and ABF (Asian Bintulu Fertilizer) in which the second plants are located in Bintulu, Sarawak. MLNG is responsible for natural gas conversion processes in gas form to liquid form before being exported. Most major LNG buyers are from electric power companies such as Japan, Korea, and Taiwan. Furthermore, the plant is responsible for producing Ammonia ABF for petrochemicals and fertilizers and urea for agricultural application in Malaysia and countries – like Asian countries.

Petronas Gas Sdn Bhd was established by Petronas in May 1983 to run the project on the Peninsular Gas Utilisation (PGU). PGU project undertaken for processing and that gas has been processed for use in Peninsular Malaysia through the pipe delivery system has been installed. Gas fields found in Terengganu were conducted by Esso Production Malaysia Incorporated under the auspices of Nippon Oil Exploration Co. Ltd.

Natural gas produced from any gas field was through separators which separate gas from oil and water. This gas then goes through a trap or isolates slugcatcher impurities found in natural gas. This clean gas was then sent to the gas processing plant GPP. At this gas processing plant, hydrocarbons are separated into methane (CH4), ethane (C_2H6), propane (C_3H_8), butane (C_4H_{10}) and condensate (C_{5++}).

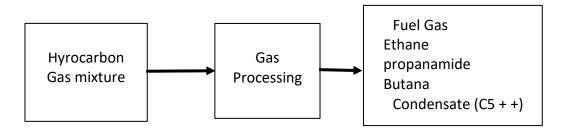


Figure 2.1 Gas Processing Plant

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Gas processing plant (GPP) is located in Kerteh, Terengganu. GPP has been designed and built to treat hydrocarbon mixture gas (natural gas) received from some of gas fields and off gas (which evolved from the crude oil reservoir tanks) from Terengganu Crude Oil Terminal (TCOT), to produce gas quality and meet the specifications market required.

The gas is processed to separate hydrocarbons and produce hydrocarbon such as ethane (C2H6), propane (C3H8), butane (C4H10) and the others in circumstances that can be sent through pipelines. Figure 2.1 displays the process sequence.

Commercial gas (methane and ethane) is sent by pipeline transmission system known as "The Peninsular Gas Utilisation Project (PGU)". Propane and butane in liquid form was sent as a mixture to the Export Terminal at Tanjung Sulong and also the Petronas Refinery (Terengganu) Sdn Bhd to tank as LPG or cooking gas for use in the local market.

2.1.1 Natural Gas Flow Process

Natural gas is any hydrocarbons or mixtures of hydrocarbons with other materials in the outlet gas from oil or gas wells. It is used as fuel. Most of the natural gas consists of methane and light hydrocarbons (C2 - C4).

Raw natural gas (natural gas) can be divided into three categories:

- Non-Associated Gas the free gas is not in contact with crude oil in the reservoir / tank. It is commonly found in gas reservoirs only.
- b. Associated gas free gas in contact with crude oil in the reservoir
- c. Soluble gas gas dissolved in crude oil in the reservoir and will be released when the pressure and temperature decrease.

Gas Processing Plant

Operation of gas processing is more difficult than oil refining. This is because each of the gas is boiling at one temperature only. With this, the column separation has many trays and involves many reboiling and refluxing. Table 2.1 shows the boiling point of the gas component in natural gas.

Table 2.1 Boiling Point for Natural Gas Component

Component	Formula	Boiling Point (@F)
Hydrogen		-423
Methane	CH ₄	-258
Ethane	C₂H ₆	-127
Ethylene	C ₂ H ₄	-155
Propane	C 3H8	-44
Propylene	C₃H ₆	-54
Iso Butane	C4H10	11
Normal Butane	C4H10	31
Iso Butylene	C ₄ H ₈	20
	C ₄ H ₈	21
Normal Butylenes	C ₄ H ₈	34
	C ₄ H ₈	39

Gas will be sent to the gas plant and goes through a process follows:

- Compression: low-pressure gas is compressed to a pressure of 200 psi and the rest of it will become liquid.
- 2. Stage of separation: Gas that has been turned into a liquid to be separated from the gas
- 3. Absorption: High-pressure gas will be sent to the rectified adsorber. (rectification is a process related with distillation). In the tray on the top of the absorber, naphtha is pumped and it will flow to the bottom of the column. The Gases which are absorbed here are propane and butane. Naphtha which contains propane and butane called fat oil, naphtha while standing on top of the column that has been absorbed propane and butane called lean oil.

- Petrochemical Technology
- 4. Debutanizing: Debutanizer separating butane and propane from naphtha. The boiling point of naphtha is 180 ° F and butane at 32 ° F, then with this temperature butane will be free from naphtha.
- Process for separating ethane which occurs at Deethenizer process temperature at -127 ° F and Depropanizer process is to separate propane at a temperature of -44 ° F from naphtha.

2.1.2 Function of Equipment in Gas Processing Plant

Function of the equipment depends on the desired process in gas processing plant design. It takes several factors, which are:

- a. Composition of the input
- b. Pressure input
- c. Temperature Input
- d. Level of pollution
- e. Type of product to be produced
- f. Rate of the proceeds
- g. Quantity of the product
- h. Specification of product

There are two sources of gas used in the gas processing plant in Kerteh:

- 1. High-pressure gas delivered by Petronas Carigali Sdn Bhd from some of the production platforms offshore to the Dew Point Control Unit to process sales gas.
- 2. Low-pressure gas from Crude Oil Terminal that is sent to the Petroleum Gas Liquefaction Unit (LPGU). This is because it produces propane and butane as well as condensate.

Gas processing plants have five major process units which are:

- Dew Point Control Unit (DPCU): Function to process the feed / entries have been through slugcatcher from gas fields.
- 2. Product Recovery Unit (PRU): Function to produces propane, butane and condensate from liquid DPCU
- 3. Liquefied Petroleum Gas Unit (LPGU): Function to process off-gas from TCOT
- 4. Acid Gas Removal Unit (AGRU): Function to removes sulfur gas sales
- 5. Glycol Regeneration Unit (GRU): Function to saturate ethylene glycol to be used for the process of dehydration (removal of water).

Overview of the process to produce natural gas from the field and from the crude oil terminal is shown in Figure 2.2.

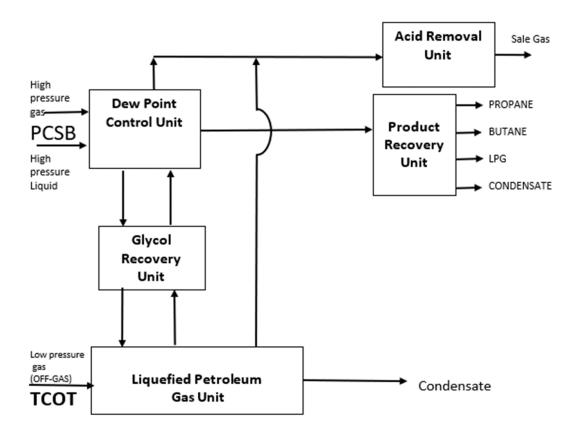


Figure 2.2 Process Flow of Gas Processing Plant (GPP, INSTEP)

2.1.3 Dew Point Control Unit (DPCU)

DPCU receives natural gas and hydrocarbon liquid from Petronas Carigali at rate 250 tan /hour. The function of this unit is to get rid of the heavy hydrocarbons from natural gas.

This process is carried out by lowering the temperature that causes heavy hydrocarbons condensed which is the exchange of gaseous to liquid. This temperature is drop by

- a. Exchange of heat by cool gas
- b. Cooling output

The expansion of natural gas is caused by the fall of the pressure, so that the temperature will also fall.

- a. Pressure drop across the valve Joule Thompson
- b. the pressure drop across the Turbo Expanders

Based on both processes above, heavy hydrocarbons and natural gas will condense at a certain temperature and pressure.

High-pressure gas with liquid from Petronas Carigali Sdn Bhd entered into the (Inlet Separator). Inlet Separator has two parts, Top Drum and Bottom Drum. Top Drum separates liquid from steam input and Bottom Drum is to separate glycol from hydrocarbons liquid. Refer Figure 2.3.

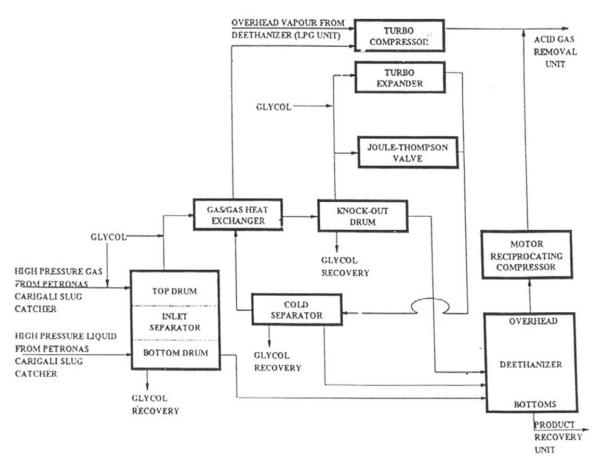


Figure 2.3 Flow Processes Occurring in Dew Point Control Unit (GPP, INSTEP)

This earlier liquid hydrocarbon was then sent to Deethanizer to separate gas sales of heavy hydrocarbons. Ethylene Glycol is injected in several parts to prevent hydrate formation (increasing the water molecules). Bottom glycol derived from the Inlet Separator Drum sent to the Glycol Regeneration Unit (GRU).

Gas from Inlet Separator flowing through the Gas Heat Exchanger which is cooled by the cold gas from Cold Separator.

Part of the condensing gas and gas is separated from the liquid hydrocarbon and glycol in Knock - Out Drum. Hydrocarbon liquids will be sent to Deethanizer. Gas from the Knock Out Drum was further cooled for condensation of heavy hydrocarbons which is still in the gas. This process occurs when the gas expands and condenses as it passes through the

Joule Thompson valve and also through the Turbo Expander depending on the amount of material processed.

Gas is once again separated from the liquid hydrocarbons in the Cold Separator. Condensed liquid is fed into gas which Deethanizer used as a cooling medium to cool the vapor / gas from the Inlet Separator by Turbo Compressor and compressed before it is sent to the sales gas pipeline at a minimum pressure through the Acid Gas Removal Unit (AGRU).

In Deethanizer, lighter components such as methane and ethane are separated from heavy hydrocarbons such as butane and above. Liquid from the bottom Deethanizer enters into the Debutanizer of Product Recovery Unit where fluid is separated into liquefied petroleum gas (LPG) (LPG consists of two main components, namely propane and butane) and condensate.

Gas / vapor coming out on top Deethenizer compressed by reciprocating Compressor Motor. The gas is mixed with the main gas line Gas Heat Exchanger and gas at the top of the Liquefied Petroleum Gas Unit (LPGU) which then into AGRU Deethanizer.

2.1.4 Product Recovery Unit (PRU)

This unit is also called, Product Procurement Unit. In this section, the feed / feed to Debutanizer is from the bottom of DPCU Deethanizer. This unit functions to produce propane, butane and condensate from liquid DPCU. Refer to Figure 2.4. Debutanizer separating LPG (mixture of propane and butane) from the condensate weight. Product from the bottom is a condensate that leaves Debutanizer and cooling down before being sent to storage or storage in On - Specification Condensate Day Tank. If the condensate is not reached pre-determined specifications, it will be sent to the condensate Flash Day Tank and then stored in the Off - Day Tank specification condensate to be treated later.

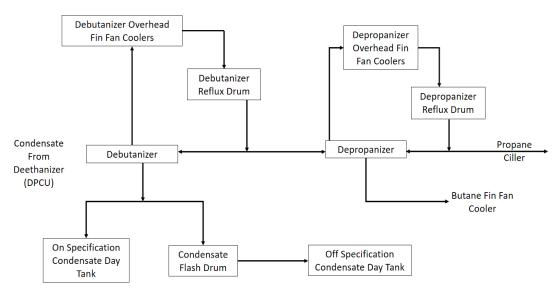


Figure 2.4 Flow Process in GE (GPP, INSTEP)

Vapor at the top from Debutanizer was fully condensed by Debutanizer Overhead Fin Fan Coolers and it is sent to Debutanizer Reflux Drum. LPG that is available in process flow will be recycled by the pump flow to Debutanizer as reflux and subsequently pumped into Depropanizer. The amount of fluid delivered to Depropenizer depending on the level of content on Debutanizer Reflux Drum. Depropanizer separating LPG from Debutanizer to propane as a product of the top and butane as a product at the bottom.

Vapor at the top of the Depropanizer Column will be cooled and all will be condensated by Fin Fan Coolers Overhead Depropanizer. As Debutanizer Overhead Fin Fan Coolers, temperature input for propane to Depropanizer Reflux Drum is controlled by the fan blades. It is then sent to the propane chiller and Coalescer for subsequent cooling. Refer Figure 2.5.

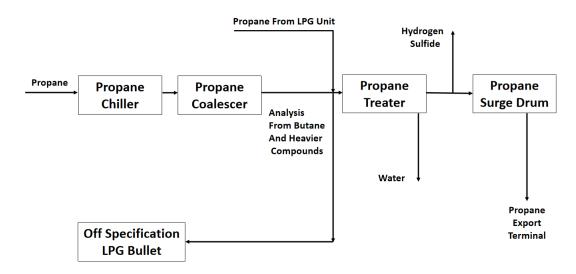


Figure 2.5 Process Flow for Propane (GPP, INSTEP)

Propane produced by Depropanizer analyzed to ensure that there is an element of butane and heavier components. If it meets the specifications, it will be mixed with propane from LPG unit to be sent to Propane Treater for drying and removing hydrogen sulfide elements and water vapor. Propane- treated and dried will be sent to propane Surge Drum before it is pumped into storage tanks Propane Export Terminal and into Refinery for marketing. For propane which does not achieve the specifications, it will be sent to Off Specification LPG Bullet and then recycled depending on the ability of the plant to operate.

Butane comes out at the bottom of Depropanizer and then cooled by Fin Fan Cooler butane and butane Coalescer. Butane will be analyzed to ensure that the content of pentane and heavier still exists. Butane which achieves specifications was mixed with butane LPG and it is sent to the butane Dryer for water removal process. While butane which does not achieve specifications will be pumped to Off-Specification LPG Bullet for recycling later.

Volume 2 Petrochemical Technology

Each product which has achieved the specifications will be transmitted/sent through pipelines to export terminals, where they are stored in Refrigerated Storage Tank.

Heat energy that is used in Debutanizer supplied by the combustion gases by Debutanizer Reboiler and Depropanizer by Depropanizer Reboiler.

2.1.5 Unit Liquefied Petroleum Gas (LPG)

Low-pressure gas from Terengganu Crude Oil Terminal (TCOT) is compressed by the compressor which consists of two stages of compression which the compressor is driven by a gas turbine. Gas received from the Knock Out Drum together with condensate will be separated. Separated gas which has been separated is compressed by TCOT Off Compressors gas and then it will be cooled before being sent to Discharge Drum. Refer to Figure 2.6.

Vapor in Drum Discharge is separated from the liquid condensation and used as feedstock for Deethanizer on LPG unit. Liquid hydrocarbons from Drum Discharge will be cooled at Discharge Cooler by cold gas from the top of the Deethanizer before being sent to the next process.

Gas from Top Deethanizer boiling separated from the liquid and the gas is then compressed by Deethanizer Overhead Compressor and mixed with salesgas from DPCU before sending them to the sales gas pipeline through the Acid Gas Removal Unit (AGRU)

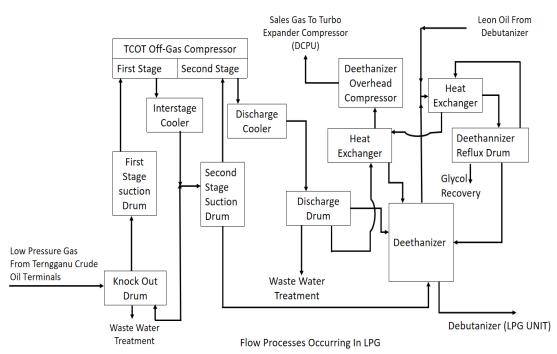


Figure 2.6 Flow Processes Occurring in LPG (GPP, INSTEP)

Product from the bottom of Deethanizer flowing into Debutanizer where LPG is separated from the condensate. Products from bottom of Debutanizer used for heating feed / feed Depropanizer in Debutanizer Bottoms / Depropanizer Feed Exchanger before it is cooled by Debutanizer Bottoms Cooler.

LPG from the top of Debutanizer will be pumped to Depropanizer where it will separate it into propane and butane. Propane is the vapor at the top of which will be condensed by the Depropanizer Condenser. Condensate Liquid was then collected in the Reflux Drum. Then it is pumped into the propane Treater (DPCU) if propane meets the specifications but if it does not meet specifications, it will be pumped into propane LPG Bullet.

Butane from Depropanizer is cooled and sent to a Butane Dryer (DPCU). For butane that is not achieving the specifications, it is pumped to the Off Specification Butane LPG Bullet.

2.1.6 Acid Gas Removal Unit (AGRU)

In the Acid Gas Removal unit, both gas from the DPU gas and LNG unit is heated in six heat exchange units and subsequently heated in the Reactor Feed Heater. Refer to Figure 2.7.

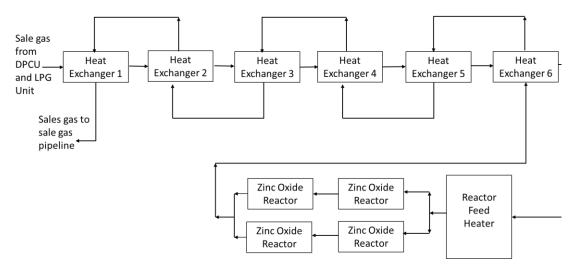


Figure 2.7 Flow Processes Occurring in AGRU (GPP, INSTEP)

This flows through the four units of the Zinc Oxide Reactor. The reactor contains zinc oxide (ZnO) which is working to absorb hydrogen sulfide (H2S) from gas. Chemical reaction is as follows:

$$371^{\circ}$$
C

 $H_2S + ZnO \longrightarrow ZnS + H_2O$

catalyst

Gas coming out of the reactor was cooled through six units of Gas Exchanger, and then flowing into the pipeline.

2.1.7 Glycol Regeneration Unit (GRU)

Rich glycol solutions (75%) were obtained from the separator drum in DPCU and LPG units combined and heated in Glycol Exchanger before it was made as a feed material / input into Glycol Feed Unit Drum. Hydrocarbon vapor dissolved will release due to rising temperatures and low pressures will be burned. Drum pressure is maintained by gas oil because glycol solution entered Column Glycol can operate at atmospheric pressure. Refer to Figure 2.8.

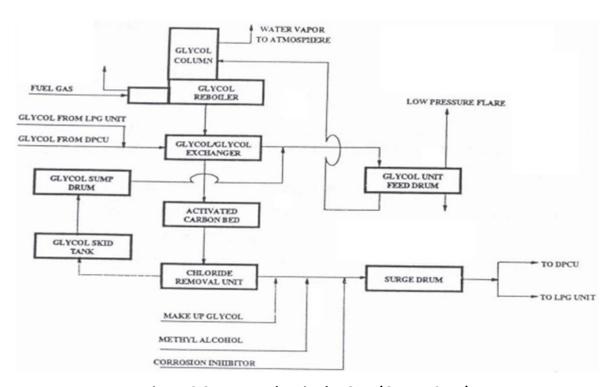


Figure 2.8 Process Flow in the GRU (GPP, INSTEP)

Rich glycol solution was concentrated to 80% earlier in the glycol columns by releasing water vapor into the atmosphere. Lean glycol solution (containing more than 25% water) is pumped through a heat exchanger to heat the rich glycol solution which has been entered in and then filtered out by the particles in Activated Carbon Bed. It is then sent to the Chloride Removal Unit where chloride in glycol solution is removed. Chloride can cause corrosion. After that, it is sent to Surge Drum. Glycol lean solution injected on some parts of the DPCU and LPG units using glycol Injection Pump.

To improve the glycol solution obtained, a chemical solution added to prevent corrosion on the inside of the pipe and also Methyl Alcohol (to prevent becoming lump due to hydration) is injected into the surge drum.

2.1.8 Product of Gas Processing Plant

In practice, some fraction of natural gas will be used in field operation, re-injected in underground reservoirs, vented or flared. The remaining fractions were processed in processing plants. Prior to processing, natural gas mostly contains methane and other varying proportions of hydrocarbons, carbon dioxide (CO₂), sulfur dioxide, nitrogen, water vapor, and helium. Gas processing will remove some of the non-methane components of natural gas to improve combustion quality such as reducing corrosion, preventing acid forming, standardizing the energy content of the gas to ensure uniform combustion in furnaces, etc.

Non-methane hydrocarbons derived during gas processing, called natural gas liquids (NGLs), liquids form more easily than methane at high pressure or low temperature. Of the NGLs, the most common are ethane, propane, and butane. Ethane and propane are further processed in large quantities to make feedstocks for plastics. While propane and butane are compressed into liquids to provide an energy-dense source of gas fuel for off-grid uses.

2.2 Oil Refinery Plant

Nowadays, there are so many refineries and petrochemical plants that operate around the world, particularly in Malaysia. An oil refinery plant is a petroleum processing plant which processes petroleum in the form of crude oil (crude oil) to produce petroleum- whether it is for domestic and international markets. Crude oil processed in our country is derived from platforms around Malaysia and some are imported from other countries such as Saudi Arabia, Indonesia and Thailand.

The key process in refineries is the fractional distillation process as well as the - other processes such as the fragmentation process and so on. Oil processing plant consists of the distillation column or separator to break off components found in crude oil into simple

components such as gasoline, kerosene, diesel, and gas naphtha - other light gases.

Apart from the fractional distillation, there is a process of fragmentation involved in oil

refineries. The purpose was to optimize petroleum-based products. Apart from the oil

produced as a vehicle fuel, there were also other byproducts produced such as sulfur,

nitrogen gas, and coke. The byproduct also has high commercial value that can give

profitable returns.

Distillation

Distillation is the key process to produce a few stages of product in the oil refinery plant.

All materials or petroleum products produced by distillation of crude oil phases. In this

operation, a large distillation column is designed in accordance with the processes

involved.

Distillation Column

Distillation columns can handle crude oil capacity between 100K - 200K barrels per day by

producing five or six components separately. Components produced in the distillation

column are gas (butane and lighter gas), gasoline, naphtha, kerosene, heavy gas oil, light

gas oil, and residue. The fractional product is as shown in Table 2.2.

Volume 2 Petrochemical Technology

40

Table 2.2 Fractional Product and Its Fractional Percentage

Fractional Product	Fractional Percentage (%)
Gas	1 – 2
Gasoline	15 – 30
Kerosene	10 – 15
Diesel/oil gas	15 – 20
Residue	40 – 50

The first element important in the distillation is charge pump, which pumps crude oil from the tank to the furnace to be heated. Crude oil delivered to the furnace to be heated up to a temperature 750°F. When heated at that temperature, some of the crude oil components form in a vapor form.

There are 53 trays in the distillation column. These trays serve to isolate and separate the crude oil cracking results. When crude oil enters the distillation column, the effects of gravity cause the heavy liquid to fall to the bottom of the distillation column while the lighter vapor will move to the top of the distillation column.

Trays in a distillation column which is perforated in which in that hole there is a Bubble caps. The aim is to convert vapor which goes through it into liquid in a concept of condensation. This occurs because of the change in temperature between the vapor and Bubble caps. So that heat transfer will happen to achieve thermal equilibrium between the vapor and tray, where steam temperature will drop, and the vapor condenses and produces liquid on Bubble caps. This fluid will be dropped and accumulated in the tray, refer Figure 2.9.

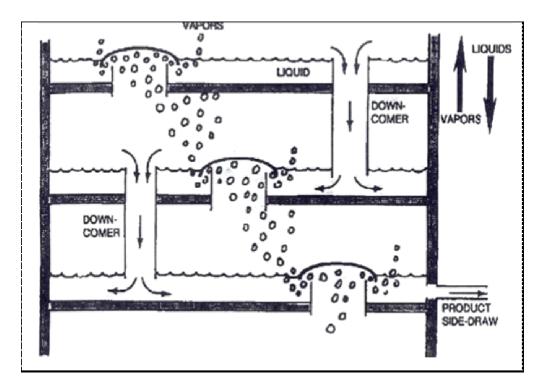


Figure 2.9 The Process of Change in Vapor to Liquid (POR, INSTEP)

The vapor condenses on the tray will continue to move to the next tray on the top of the distillation column where the same process occurs for each tray. Condensation process will continue as long as there is still crude oil entering into the distillation column. So that the amount of fluid produced and accumulated in the tray increases. To ensure that the liquid produced and collected in the excess tray flows to the other side of the downside tray, down comer is attached to the tray.

During the condensation process, there are light components that were condensed together with heavy components. So, these lightweight components will vaporize back. This occurs because the condensed liquid will be collected on a bottom tray. When liquids flow down to the bottom where distillation temperature will be higher when go through down along the tray. So this allows the lighter components to vaporize back and get on to the condenser. The liquid production and accumulation in the tray will be vented through slide draws. This process will continue until whole products are obtained.

Reflux and Reboil

There are also other processes that occur in a distillation column. To ensure that the heavy component does not fall into the upper tray, some of the vapour which comes out will vent to the coolant. Gas passing through the coolant will partially condense. Condensation products will be channeled back into the tray below. Non-condensing components will be released in the form of vapor as a distillation product. These processes are continuous, and it is called reflux.

Another situation is where the light components were condensed together with heavy components on the lower tray. So slide Draws may be used to recycle the liquid through the heater (heater) to reproduce light hydrocarbons in the distillation column as vapor. This process is called reboil.

Cut Points

An analysis of the distillation is the cut point. Cut point is a temperature where some components of distillation yield can be separated. Generally, the initial temperature for yield begins to boil named initial boiling point (IBP). While the temperature when oil 100% vaporized name the end point (EP).

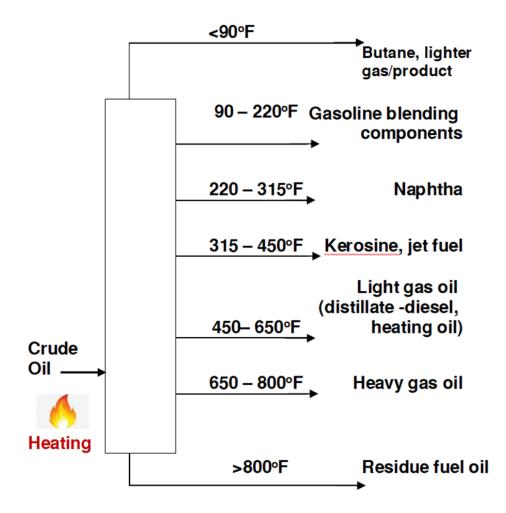


Figure 2.10 The Fractional Distillation of Crude Oil
Adapted from U.S. Energy Information Administration (EIA, 2020)

Figure 2.10 above shows distillation products with temperature that show a range of boiling temperature for each component in crude oil. For example, we have seen gasoline with a temperature range 90°F - 220°F, from that temperatures, initial boiling point (IBP) for gasoline is 90°F and the end point (EP) is 220°F. Let us compare between gasoline and naphtha, we find that the initial boiling point (IBP) for naphtha is the end point (EP) for gasoline while the end point for naphtha, is an initial boiling point of kerosene and so on.

2.2.1 Flow Process of Oil Refinery Plant

According to Figure 2.11, the basic flow process in oil Refinery Plant are Separation, Conversion and Storage and blending.

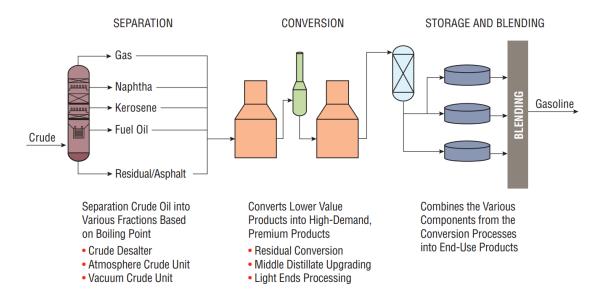


Figure 2.11 Basic Flow Refinery Process Flow (Flowserve, 2019)

Separation

Refinery begins with separation process with distillation, separate fraction, or cuts. Various types of distillation columns will be used based on desired products. The distillation column uses to heat liquid into vapour and lift upward to be distilled again into separated substances. Smaller molecules vaporize at lower temperatures, so crude oil can be distilled to separate out the different hydrocarbons.

Trays fixed in the column allows heated vapour to rise and collect at different temperature levels, separating out the various liquids derived from crude oil (see Figure 2.10). Column at the top is cooler than the bottom, as liquids vaporize and rise, then condense again, flowing out onto their respective trays. Butane and other light products rise to the top of the column, while straight-run gasoline, naphtha, kerosene, diesel, and heavy gas oil gather on the trays, leaving straight run residue at the base of the column. A group of

Volume 2 Petrochemical Technology

"heavy or light" liquids are based on their specific gravity, which is determined based on its weight and density compared to that of water (API org, 2021).

Conversion

In conversion processes, the size structure of hydrocarbon molecules will be changed by:

- Decomposition: breaking down the larger molecules into smaller molecules with lower boiling points through cracking and related processes.
- Unification: Building small molecules into larger molecules through alkylation, polymerization, and related processes.
- Reforming: Rearranging molecules into different geometric structures in isomerization, catalytic reforming, and related process.

Cracking is widely used in the conversion process because it uses heat, pressure, catalysts, and sometimes hydrogen to crack heavy hydrocarbon molecules into lighter ones. A cracking unit consists of one or more tall, thick-walled, rocket-shaped reactors and a network of furnaces, heat exchangers, and other vessels. Advanced and complex refineries may have more types of crackers, including fluid catalytic cracking units and hydrocracking/hydrocracker units (EIA ,2020).

Treatment processes prepare hydrocarbon streams for additional processing and prepare finished products using chemical or physical separation. Processes include desalting, hydrodesulfurization, solvent refining, sweetening, solvent extraction, and dewaxing (Gary et al., 2007). Treatment is finishing touches occurred during the final treatment. To make gasoline, refinery technicians carefully combine a variety of streams from the processing units. Octane level, vapor pressure ratings, and other special considerations determine the gasoline blend.

Storage and Blending

Lastly, blending is the process of mixing and combining hydrocarbon fractions, additives, and other components to produce finished products with specific performance properties. Other refining operations include light-ends recovery, sour-water stripping, solid wastes and wastewater treatment, process-water treatment and cooling, storage and handling, product movement, hydrogen production, acid and gas treatment and sulphur recovery.

2.2.2 Function of Equipment in Oil Refinery Plant

In general, there are five categories of oil refinery process associated operations as displays in Table 2.3 (Petroleum Refining, 2021).

Table 2.3 Process Category and its operation in Oil Refinery Plant

Item	Process	Operation
1	Separation processes	a. Atmospheric distillationb. Vacuum distillationc. Light ends recovery (gas processing)
2	Conversion processes	 a. Cracking (thermal and catalytic) b. Reforming c. Alkylation d. Polymerization e. Isomerization f. Coking g. Visbreaking
3	Treating processes	a. Hydrodesulfurizationb. Hydrotreatingc. Chemical sweeteningd. Acid gas removale. Deasphalting
4	Feedstock and product handling	a. Storageb. Blendingc. Loadingd. Unloading
5	Auxiliary facilities	a. Boilersb. Wastewater treatmentc. Hydrogen productiond. Sulphur recovery plant

Volume 2 Petrochemical Technology

Separation Process

The first phase in petroleum refining operations is the separation of crude oil into its major constituents using 3 petroleum separation processes: atmospheric distillation, vacuum distillation, and light ends recovery (gas processing). The main contents of crude oils are a mixture of hydrocarbon compounds including paraffinic, naphthenic, and aromatic hydrocarbons with small amounts of impurities including sulphur, nitrogen, oxygen, and metals. Refinery separation unit processes separate these crude oil constituents into common boiling-point fractions products.

Conversion Processes

Conversion unit is used to meet the demands for high-octane gasoline, jet fuel, and diesel fuel, components such as residual oils, fuel oils, and light ends. Here fraction products are converted to gasoline and other light fractions. Processes such as cracking, coking, and visbreaking are used to break large petroleum molecules into smaller groups. Polymerization and alkylation processes are used to combine small petroleum molecules into larger ones. Isomerization and reforming processes are applied to rearrange the structure of petroleum molecules to produce higher-value molecules of a similar molecular size.

Treating Processes

In treating, petroleum is treated to stabilize and upgrade petroleum products by separating them from less desirable products and by removing objectionable elements. Unwanted elements such as sulfur, nitrogen, and oxygen are extracted away (removed) by hydrodesulfurization, hydrotreating, chemical sweetening, and acid gas removal. Treating processes, employed primarily for the separation of petroleum products, include such processes as deasphalting. Desalting is used to remove salt, minerals, grit, and water from crude oil feedstocks before refining. Asphalt blowing is used for polymerizing and stabilizing asphalt to improve its weathering characteristics.

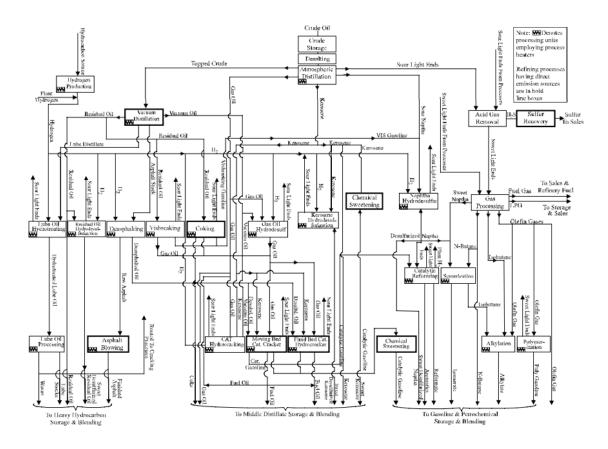


Figure 2.11 Integrated flow process of petroleum refinery

(Source: Petroleum Refining, https://www3.epa.gov/ttnchie1/ap42/ch05/final/c05s01_2015.pdf industry)

Feedstock and Product Handling

The refinery feedstock and product handling operations consist of unloading, storage, blending, and loading activities.

Auxiliary Facilities

A wide assortment of processes and equipment not directly involved in the refining of crude oil is used in functions vital to the operation of the refinery. Examples are boilers, wastewater treatment facilities, hydrogen plants, cooling towers, and sulphur recovery units. Products from auxiliary facilities (clean water, steam, and process heat) are required by most process units throughout the refinery.

2.2.3 Refining Product and Their Usage

Raw material of crude oil and intermediate materials are processed at refineries into these products which are:

- gasoline
- distillate fuel oil (diesel fuel, home heating oil, industrial fuel),
- jet fuels (kerosine and naphtha types),
- residual fuel oil (bunker fuel, boiler fuel),
- liquefied petroleum gasses (propane, ethane, butane),
- coke and kerosine.

About 90% crude oil is converted to fuel products, while nonfuel products such as asphalt, road oil, lubricants, solvents, waxes and nonfuel coke, and petrochemicals and petrochemical feedstock such as naphtha, ethane, propane, ethylene, propylene, butylene, benzene, toluene, and xylene comprise the remaining crude conversion (Gary et a al., 2007).

Usage of Some Refinery Products

Petroleum industry used to characterize products by the number of carbon atoms and saturated bonds in the molecule.

Low-boiling Products

Low-boiling products are classified with compounds that are in the gas phase at ambient temperatures and pressures such as methane, ethane, propane, butane, and corresponding olefins. As seen in Figure 2.12 shows respective boiling temperatures for each refinery product.

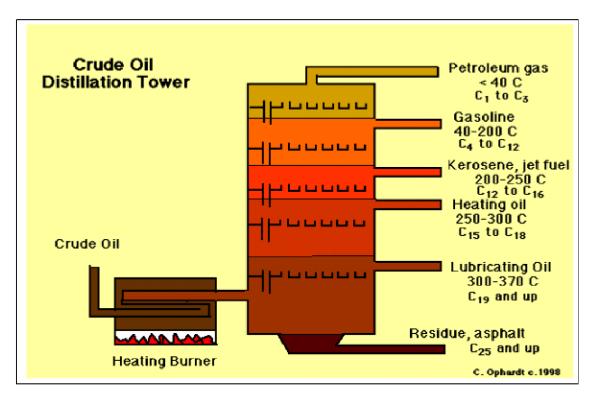


Figure 2.12 The Fractional Distillation of Crude Oil (Windrush Interactive Publication, 2016)

Methane (C1) can be used as feedstock for hydrogen production by pyrolytic cracking and reaction with steam. Ethane (C2) can be used as refinery fuel or as feedstock to produce hydrogen and ethylene in petrochemical plants. Propane (C3) usually used as a refinery fuel but also sold as a liquefied petroleum gas (LPG). In some locations, propylene is separated for sale for polypropylene. Butane is present in crude oils and produced by refinery processes are used as components of gasoline and refinery processing as well as in LPG.

Gasoline

Gasoline in most refineries produces three grades (unleaded regular, premium, and superpremium) and in addition, supply a leaded regular gasoline to meet the needs of farm equipment and some automobiles. The principle between regular and premium is the antiknock performance.

Volume 2 Petrochemical Technology

Distillate fuels are products that can be divided into three types: Jet or turbine fuels, automotive diesel fuels, railroad diesel fuels and heating oils. These products are blended from a variety of refinery streams to meet the desired specification.

Residuals Fuel Oils

Light residue oil is used for furnaces with burners that can atomize oil with higher viscosity. It may require preheating in order to vaporize it in a spray-nozzle burner when stored at low temperatures

Heavy residual fuel oil composes heavy parts of crude and fractionating tower bottoms from vacuum distillation, and it sells for a very low price for its viscosity and sulphur content. Heave residual oil usually used for ships.

Activity 2.0 Review Questions

- State and explain the three categories of raw natural gas produced from production wells
- 2. State five factors that are taken into consideration in the design of a gas processing plant
- 3. State two sources of gas processed in the gas processing plant in Kerteh
- 4. Describe 5 important unit in GPP
- 5. Describe the main functions of the DewPoint Control Unit (DPCU) in a GPP. Explain how the operation works.
- 6. Show the chemical reactions which occur in Acid Gas Removal Unit (AGRU) to remove hydrogen sulphide gas.
- 7. Describe how a distillation column works?
- 8. List the component produce in distillation column.
- 9. List the fractional products and their fractional percentage.
- 10. Draw a distillation column and each component produced after the process.
- 11. Explain the term reflux, reboil and cut points.
- 12. Explain the flow process of oil refinery plant.
- 13. Draw the basic flow process of refinery plant.
- 14. What is conversion process?
- 15. What is the equipment for cracking?
- 16. List the equipment in gas processing plant.
- 17. List the operation equipment in oil refinery plants.
- 18. Explain the basic processes in the oil refining plant.
- 19. Describe terms of Separation, Conversion, Storage and Blending in oil refinery plants.
- 20. What is Treating during refinery processing and name of the product produced.

Petrochemical Plants

3.0 Petrochemical Plants

Petrochemical plants produce petrochemicals which are chemical products that have been converted from natural resources like petroleum or crude oil. Methane (sales gas for power generation), ethane, propane, butane and condensates are obtained from natural gas and used as feedstock for the petrochemical industry. A wide range of petrochemical produced in Malaysia shown in Table 3.1:

Table 3.1 Some of Petrochemical Product in Malaysia

Petrochemical Product		
Ethylene	Propylene	Methyl Tertiary –Butyl Ether (MTBE)
Methanol	Polypropylene (PP)	Linear Low Density Polyethylene (LLDPE)
High Density Polyethylene (HDPE)	Acrylic Acid	Polyethylene
Ammonia	Urea	Heavy Glycol (HG)
Ethylene Oxide	Ethylene Glycol	Ethanolamines
Alkoxylates / Functional Fluids	Butanol	Glycols Ethers
Butyl Acrylate	Butyl Acetate	Benzene
Toulene	Xylene	Liquefied Natural Gas (LNG
Tri Ethylene Glycol (TEG)	Di Ethylene Glycol (DEG)	Mono Ethylene Glycol (MEG)
Polystyrene	Styrene Monomer	Acetic Acid

The first petrochemical plants in Malaysia started as early as 1973 with the production of polyvinyl chloride (PVC) and subsequently of polystyrene (PS) resin based on imported monomers in Johor and PBC plant in Penang. Later, the petrochemical industry began to grow rapidly in the 1990s with the founding of first polypropylene plant by Titan Group in Johor.

Major petrochemical companies in Malaysia are:

- a) PETRONAS Chemicals Group Berhad
- b) Lotte Chemical Titan
- c) BASF PETRONAS Chemicals Sdn Bhd
- d) Idemitsu Chemicals
- e) Toray Plastics

Petrochemical plants exist in numerous locations in Malaysia. Major petrochemical zones in Malaysia are:-

- Kertih Integrated Petrochemical Complex (KIPC), Terengganu focuses on ethylene based products.
- Gebeng Integrated Petrochemical Complex (GIPC) Pahang focused on propylene based products.
- Pasir Gudang-Tanjung Langsat Petrochemical Zone, Johor are naptha based. The naptha cracker in Pasir Gudang-Tanjung Langsar produces ethylene, propylene as feedstocks for the production of polypropylene and polyethelene.
- Pengerang Integrated Petroleum Complex (PIPC) Johor, which include oil refineries,
 naptha crackers and petrochemical plants as well as LNG import terminal and
 regasification plant.
- Sipitang Oil and Gas Industrial Park (SOGIP) is strategically located within Sabah,
 Brunei and Labuan region. This park consists of an ammonia plant, urea plant and a granulation plant as well as utilities and jetty facilities.
- Other petrochemical plants in Malaysia including
 - the ammonia and urea plants in Bintulu, Sarawak and Gurun, Kedah;
 - acrylonitrile butadiene styrene (ABS) plant in Penang
 - nitrile-butadiene rubber (NBR) plants in Kluang and Pasir Gudang, Johor

3.1 Methyl Tertiary -Butyl Ether (MTBE) and Polypropylene Plant

Methyl Tertiary –Butyl Ether or MTBE is an organic compound with the formula $C_5H_{12}O$. MTBE is produced as a by-product of petroleum refinery by combining methanol and isobutylene. MTBE is a flammable, clear, colourless liquid with a low viscosity. MTBE is not toxic and is not harmful to health. MTBE is a toxicological where if swallowed, by skin contact or inhalation in large quantities, the effect is just like contact with petrol.

The properties of MTBE is given in Table 3.2.

Table 3.2 Properties of MTBE (Hamid & Ali, 2004)

Characteristic	Information
Chemical Name	Methyl Tertiary –Butyl Ether
Chemical Formula	C₅H ₁₂ O
Chemical Structure	CH ₃ CH ₃ CH ₃ CH ₃ CH ₃
Molecular Weight	88.15
Boiling Point	55°C
Freezing Point Point	-108.6 °C
Density at 20°C	0.74 g/m ³

Propylene (C_3H_6) also known as propene in IUPAC nomenclature is the second most important product in the petrochemical industry after ethylene. Propylene is non-corrosive, non-toxic and colourless gas with little odor. The properties of propylene are given in Table 3.3.

Table 3. 3: Properties of Propylene (Wells, 1991)

Characteristic	Information
Chemical Name	Propylene or propene
Chemical Formula	C₃H ₆
Chemical Structure	HC=CCH3
Molecular Weight	42.08 g/mol
Boiling Point	-47.6 °C
Density of liquid at 20°C	0.508 g/m ³

Polypropylene is made from propylene through a polymerization process in the presence of a catalyst. Polypropylene is a polyolefin which is light weight with high optical clarity and low moisture vapour transmission. It has a very good resistance to acids, alkalis and inorganic chemicals. It has low density, high hardness and abrasion resistance. Table 3.4 shows the properties of polypropylene.

Table 3.4: Properties of Polypropylene

Characteristic	Information
Elongation	500 – 900 %
Tensile Strength	29.3-38.6 MPa
Melting Temperature	170-172°C
Density at 20°C	0.88-0.91 g/m ³

MTBE and Polypropylene Plant In Malaysia

The petrochemical plant in Malaysia which producing MTBE, propylene and polypropylene are as follow (MIDA, 2020):-

- Petronas Chemicals MTBE Sdn Bhd , located at Gebeng, Kuantan. This plant can produce MTBE at 300 000 tonnes per year and 80 000 tonnes/year of propylene.
- Pengerang Refining and Chemical (PrefChem) located at Pengerang, Johor. This plant can produces 550 000 tonnes/year of MTBE. PrefChem also will have two polypropylene plants that are expected to be operated on September 2021. Each of this polypropylene plant has a capacity to produce 450,000 tonnes/year of polypropylene.P refChem Polypropylene Plants are using licensor technology from Lyondell Basell. PrefChem also will be able to produce 630 000 tonnes/year of propylene from it's propylene plant.
- Lotte Chemical Titan (M) Sdn Bhd located at Pasir Gudang, Johor. The Titan Groups set up the first polypropylene plant in Malaysia and went operation in the early 1990. It have three polypropylene plants (PP1, PP2 and PP3), which can produce 640 000 tonnes/year of polypropylene. PP1 and PP2 are using licensor technology from Lyondell Basell. While it's propylene plant have a capacity to produce 280 000 tonnes/year of propylene.
- Petronas Chemical Olefins Sdn Bhd, located at Kerteh, Terengganu has a propylene plant which can produce 95 000 tonnes/year of propylene.

MTBE and Polypropylene Production Process

The process of MTBE plant and Polypropylene contains 8 units of processes shown in Figure 3.1:

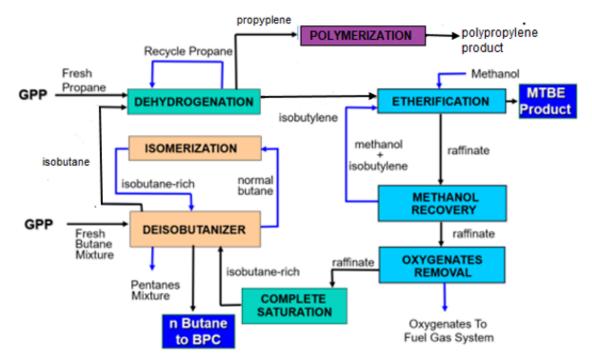


Figure 3.1 Block Flow for MTBE and Polypropylene Plant

1) Deisobutanizer

Deisobutanizer is a distillation column for separating butane / butane and isobutene / isobutene from a mixture of natural gas supplied by Petronas Gas Berhad. Isobutene is sent directly to the dehydrogenation unit while butane is sent to the Isomerization Unit. Apart from butane and isobutene will be sent to the Fuel Gas System to be a mixture of pentane by product.

2) Isomerization

Isomerization is for converting normal butane in the form of a straight chain to isobutene in the form of branched chains. Production of Isobutene will be sent back to the Deisobutanizer Unit.

3) Dehydrogenation

Isobutane and propane are fed to the dehydrogenation unit. Dehydrogenation is to convert isobutene to isobutylene by removing two units of hydrogen atoms from molecules isobutene to produce isobutylene before sending it to the Etherification unit.

Catalyst: Platinum

Dehydrogenation is also used to produce propylene / propene from propane mixture which is next to be sent to Polymerization (Polypropylene Plant).

4) Polymerization

Propylene from the dehydrogenation unit is fed into the polymerization unit. Polymerization is producing polypropylene which carries out the combination reaction between propylene chains.

5) Etherification

Etherification is the most important unit for MTBE plants in which there will be a reaction between isobutylene with methanol to produce MTBE. Methanol is obtained from Petronas Methanol Labuan.

6) Methanol Recovery

Methanol recovery is to recover unreacted methanol with isobutylene in Etherification Unit and also the components which are not produce MTBE. Recovery Methanol will be sent back to the Etherification unit, while the components that do not produce MTBE will be sent to Oxygenate Removal Unit.

7) Oxygenate Removal

Oxygenate Removal is to remove the oxygenate (components, which contain oxygen) and isobutylene. Oxygenate will be sent to the Fuel Gas System while the unreacted isobutylene will be sent to the unit Complete Saturation.

8) Complete Saturation

Complete saturation is to produce the isobutene by performing the reaction with hydrogen gas. Isobutene will be sent back to De-isobutanizer Unit.

Application of MTBE

The application of MTBE are as follow (Petronas, 2021):

- Gasoline blending for higher RON grade gasoline.
- Manufacturing of electronic displays (flat screen television, mobile phone screen).
- Synthetic rubber tire manufacturing within the automotive industry.
- Fragrances and flavour compositions for imitation of lemon, grapefruit, orange, mint for pharmaceuticals, cosmetics, oral & consumer products.
- Pharmaceutical applications.
- Paint thinner blending.

Application of Polypropylene

The application of polypropylene are as follow (Petronas, 2021):-

- Plastic for the food industry and housewares.
- Interior trim and bumper system for automotive industry.
- Toys production.
- Insulation material for electrical cables.
- Grid type flooring for sport facilities.

3.2 Ethylene and Polyethylene Plant

Ethylene is one of the most important petrochemical intermediates and is a feedstock for various products. It is a colourless, flammable gas with a faint "sweet and musky" odour when pure. It is the simplest alkene and is widely used in the chemical industry. Chemical formula for ethylene, C₂H₄. Table 3.5 shows the properties of ethylene (Wells, 1991).

Table 3.5 Properties of Ethylene

Characteristic	Information
Chemical Name	Ethylene or ethene
Chemical Formula	C ₂ H ₄
Chemical Structure	C = C
Molecular Weight	28.05 g/mol
Melting Point	-169.2 °C
Boiling Point	-103.7°C
Density of liquid at 0°C	0.98 g/m³

Polyethylene has the simplest structure of all polymers. The chemical formula for polyethylene is $(C_2H_4)n$. Polyethylene can be classified into; Low Density (LDPE), Linear Low Density Polyethylene (LLDPE), Middle Density Polyethylene (MDPE) and High Density Polyethylene (HDPE). Polyethylene is low at strength but high in ductility and impact strength. It is also low in hardness and rigidity but also low in friction.

Volume 2 Petrochemical Technology

Ethylene and Polyethylene Plant In Malaysia

The petrochemical plant in Malaysia which producing ethylene and polyethylene are as follow (MIDA, 2020):-

- Petronas Chemicals Ethylene Sdn Bhd, located at Terengganu. This plant can produce
 400 000 tonnes/year of ethylene
- Petronas Chemicals Olefins Sdn Bhd, located at Terengganu which can produce ethylene at a capacity 600 000 tonnes/year.
- Pengerang Refining Company Sdn Bhd Pengerang, located at Johor. This plant produces LDPE at capacity 350 000 tonnes/year and HDPE at capacity 400 000 tonnes/year using LyondelBasell Hostalen Advanced Cascade Process (Hostalen ACP) technology.
- Lotte Chemical Titan (M) Sdn Bhd, located at Johor. Lotte Chemical Titan has three polyethylene plants (PE 1, PE 2 and PE 3 with the production capacity 565 000 tonnes/year of polyethylene. PE 1 is producing LDPE using Exxon Mobil licensor technology, while PE 2 is producing HDPE using Mitsui licensor technology and PE 3 is producing LDPE and HDPE using Univation licensor technology.

3.2.1 Ethylene Processing Plant

Ethylene plant receives gas containing ethane after it is separated from natural gas at the Gas Processing Plant (GPP). Process flow of ethylene plant shown in Figure 3.2.

1) Acid Gas Removal

Gas that contains ethane, enters into the plant through the first part of the Acid Gas Removal. This section has two columns that remove acidic gases to acid flare.

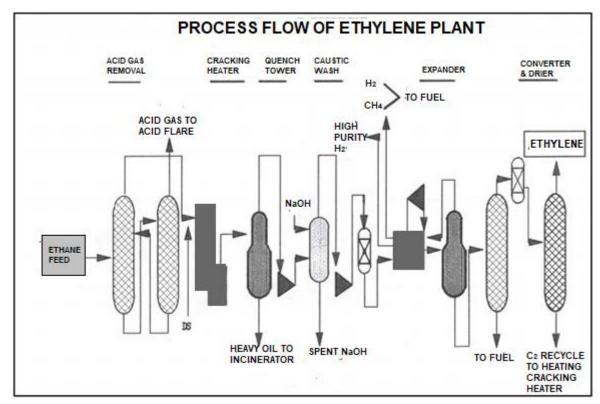


Figure 3.2 Process Flow of Ethylene Plant

2) Cracking Heaters

After that it flows into cracking heaters. In this section, the hydrocarbons are cracked into smaller molecules producing ethylene and it's co-products.

3) Quench Tower

Cracked gases cooled in the quench tower to preserve the current composition of the gas and prevent undesirable side reactions from taking place.

4) Caustic Wash

In Caustic Wash, the remaining gases are treated with a caustic soda solution to remove any sulphurous gases and carbon dioxide.

4) Expander

It is then compressed by a multistage compression system to achieve an adequate pressure to separate hydrocarbon from water (H₂O).

6) Dryer

The cracked gases are dried to remove the moisture in the gases before going to the converter to prevent the formation of hydrates and ice.

7) Convertor (Fractionation)

The convertor section receives the compressed cracked gas for further fractionation into different products. In the first column (demethanizer), methane and hydrogen are removed. These gases are either burnt as fuel or purified prior to sale.

From the bottom of the demethanizer, containing ethylene and heavier products are fed into a second column (deethanizer) where acetylene, ethylene and ethane are separated overhead. At deethanizer overhead, it is heated and hydrogenated to convert acetylene to ethylene and ethane. Then ethylene and ethane is fed to the ethylene fractionator (C2 splitter).

Ethylene is drawn from the top of the fractionator column, while Ethane, from the bottom column, is recycled to the cracking heater. The deethanizer bottom stream is fed to a depropanizer, which distills C3 components.

3.2.2 Polyethylene Processing Plant

The polyethylene plant receives raw materials from the ethylene plant. This plant generally consists of seven major operation units as shown in Figure 3.3.

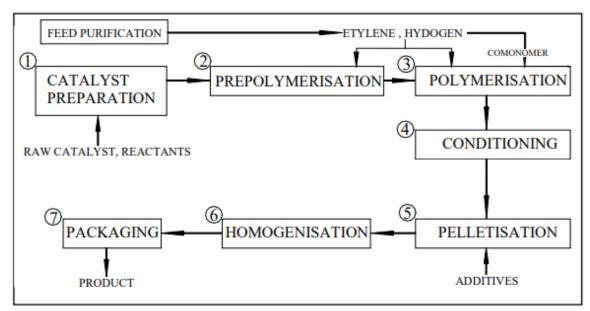


Figure 3.3 Block Flow Diagram of Polyethylene Plant

1) Catalyst Preparation

Catalyst Preparation Unit produces a highly active catalyst of Titanium chemical compounds and also produces a mixture of Organo-Magnesium (Ziegler). It also serves to activate the catalyst of raw Chromium.

2) Pre polymerisation

Pre-polymerisation produces the particle catalyst coated with PE powder (prepolymer Powder) to achieve the particle size in required level for the distribution of the process.

3) Polymerisation

Polymerisation Unit is to produce the required polyethylene in the powder form.

4) Conditioning

Conditioning Unit is maximizing the efficiency of gas use in this process through acquisition and usage of the inlet gas. It also serves to remove residual hydrocarbons and catalyst residue which is no longer active.

5) Pelletisation

Pelletisation is to convert dry polymer powder form to pallet form for safety and easy to handle. In this unit additive was added to improve product characteristic.

6) Homogenisation

Homogenisation unit in airtight condition is used as a place for the products mixed and blended before being sent to an airtight storage unit.

7) Packaging

Packaging serves to wrap pallets from airtight storage and put it in a bag before being sent to the warehouse for sales purposes.

Application of Ethylene and Polyethylene

Ethylene is the raw material used in the manufacture of Polyethylene (PE), Mono Ethylene Glycol (MEG), Ethylene Dichloride (EDC), Ethylbenzene and Vinyl Acetate Monomer (VAM).

These products are used in a wide variety of industrial and consumer markets such as:

- Packaging
- Transportation
- Electrical/Electronic
- Textile
- Construction Industries
- Consumer Chemicals
- Coatings
- Adhesives

Application of LLDPE and LDPE are more preferable to the electrical insulation. While application of HDPE, for making household chemical containers and drums in industrial packaging and also in the piping industry.

3.3 Ammonia and Urea Plant

Ammonia is a compound of nitrogen and hydrogen with the formula NH₃. It is colourless gas with a characteristic pungent smell. Ammonia is stored as a pressurised gas at -5 to +5°C, or in a liquid form at -33°C. The properties of ammonia are shown in Table 3.6 (Wells, 1991)

Table 3.6 Properties of Ammonia

Characteristic	Information	
Chemical Name	Ammonia	
Chemical Formula	NH ₃	
Chemical Structure	H N H	
Molecular Weight	17.03	
Melting Point	-77.7°C	
Boiling Point	-33.4°C	
Density at 20°C (gas)	0.7771 g/m ³	

While urea known as carbamide is an organic compound with the chemical formula $CO(NH_2)_2$. It is an odourless solid that is highly soluble in water. The properties of Urea are shown in Table 3.7 (Wells, 1991).

Table 3.7 Properties of Urea

Characteristic	Information	
Chemical Name	Urea	
Chemical Formula	CO(NH ₂) ₂	
Chemical Structure	H_2N NH_2	
Molecular Weight	60.06	
Melting Point	-132.7°C	
Boiling Point decomposers		
Density at 20°C (gas)	1.323 g/m ³	

Ammonia and Urea Plant in Malaysia

The Ammonia and Urea Plant in Malaysia are:

- a) Petronas Chemical Fertiliser (Kedah) Sdn. Bhd (PCFK is located at Gurun Kedah. This plant can produce 400 000 tonnes/year of ammonia and 696 000 tonnes/year of urea.
- b) Petronas Chemicals Fertiliser Sabah Sdn. Bhd (PCFSSB), located at Sipitang, Sabah. This plant can produce 770 000 tonnes/year of ammonia and 1 270 000 tonnes/year of urea.
- c) Asean Bintulu Fertiliser Sdn. Bhd (ABF) located at Bintulu Sarawak. This plant can produce 450 000 tonnes/year of ammonia and 750 tonnes/year of urea.
- d) Petronas Chemicals Ammonia Sdn. Bhd. (PCASB) located at Kertih, Terengganu. This plant can produce 450 000 tonnes/year of ammonia.

3.3.1 Ammonia Processing Plant

Ammonia is produced by the reaction of hydrogen (from natural gas) and nitrogen (from the air) under pressure. First, gas mixture of hydrogen and pure nitrogen in a ratio of 3:1 is provided.

Natural gas contains methane and hydrocarbon vapour as well as impurities and inert material used as a raw in the preparation of hydrogen-nitrogen mixture for ammonia synthesis.

Impurities such as carbon particles and sulphur compounds are removed from natural gas received from crude oil terminal storage processes. Later, it was converted to a gas mixture containing mostly hydrogen gas, carbon monoxide and carbon dioxide.

Nitrogen was incorporated into vapour gas by adding an optimum quantity of air between the two stages of recovery. A few purification steps are required to obtain a suitable hydrogen and nitrogen mixture for the ammonia synthesis process. Normally, the ammonia plant is built alongside with the urea plant because ammonia products from the ammonia plant is sent directly to the urea plant for processing. Reaction of ammonia production briefly shown as follows:

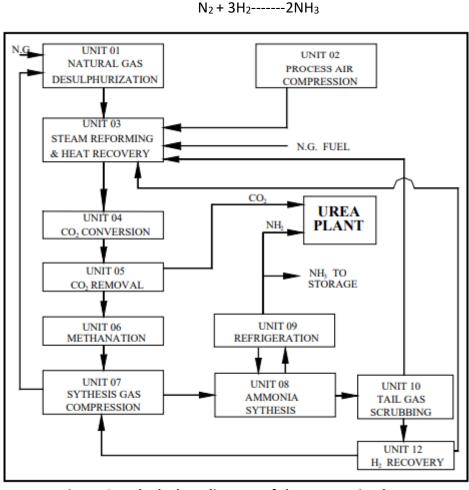


Figure 3.4 Block Flow diagram of the Ammonia Plant

Figure 3. 4 shows the block flow diagram of Ammonia Plant. Ammonia is produced when the nitrogen and hydrogen react in the presence of the catalyst to form ammonia.

1) Desulphurization or Sulphur Removal

Natural gas that contains methane, hydrocarbon vapour and impurities such as sulphur undergo the process of sulphur removal in desulphurization unit. Sulphur needs to be removed because sulphur has an adverse effect on the catalyst used in the reforming and synthesis reaction.

Volume 2 Petrochemical Technology

2) Primary Reforming

After desulphurization, the natural gas enters into the primary reformer for steam reforming. In this reformer, 70% of feed natural gas is converted to hydrogen, carbon monoxide and carbon dioxide. The reaction is as follows;

$$CH_4 + H_2O$$
 ----- $CO + 3H_2$
 $CH_4 + 2H_2O$ ----- $CO_2 + 4H_2$

3) Secondary Reforming

The gas mixture (synthesis gas) from the primary reformer enters a secondary reformer, where the methane residual is formed by exposure to compressed air. The air also provides the nitrogen required to produce ammonia.

After secondary reforming, the process gas contains hydrogen, nitrogen, carbon monoxide, carbon dioxide and residual methane.

4) Shift Conversion / CO₂ Conversion

Gas from Secondary reformer is sent to the CO_2 Conversion Unit where carbon monoxide produced in the reforming stage is removed by converting it to carbon dioxide. The gas next goes to the absorber for removal of CO_2 .

5) CO₂ Removal

The synthesis gas is purified by removing carbon dioxide via absorption with hot liquid potassium carbonate.

Absorbed carbon dioxide will be used as raw material for the production of urea and a small portion was released into the atmosphere.

6) Methanation

There will be a trace amount of carbon monoxide and carbon dioxide in the synthesis gas, which will be removed and converted back to methane (CH_4) in the methanator.

7) Synthesis Gas Compression

In a multistage compressor, with the required pressure, the synthesis gas (CH₄) from the Methanator is compressed to become liquid for ammonia synthesis.

8) Ammonia synthesis reactor

Clean synthesis gas with a hydrogen-nitrogen ratio of 3:1 compressed to 300 bar and passed through a catalytic reactor to produce ammonia synthesis.

The ammonia synthesis reaction between nitrogen and hydrogen is given as below:

$$N_2 + 3H_2 - - - 2NH_3$$

9) Refrigeration

Ammonia vapour from the reactor is condensed and converted into liquid ammonia under pressure of 300 bar coolant by water. While some ammonia is condensable with refrigerant. Production of ammonia is also sent to the urea plant for the urea production or to the storage tank.

10) Tail Gas Scrubbing

Flash gas and purge gas from the Synthesis Unit which still contains ammonia is absorbed in the Tail Gas Scrubbing Unit and then sent to the ammonia recovery unit or used as fuel for the heating of the primary reformer.

3.3.2 Urea Processing Plant

The Urea processing plant used liquid ammonia and carbon dioxide as a raw material. The chemical equation for the preparation of urea is as follows:

 $2NH_3 + CO_2 - NH_2COONH_4$ (ammonium carbamate)

NH₂COONH₄ -----NH₂CONH₂ (urea)+ H₂O

The ammonia and carbon dioxide react to form ammonium carbamate, a portion of which dehydrates urea and water. Figure 3.5 shows the Process Flow Diagram of Urea Plant.

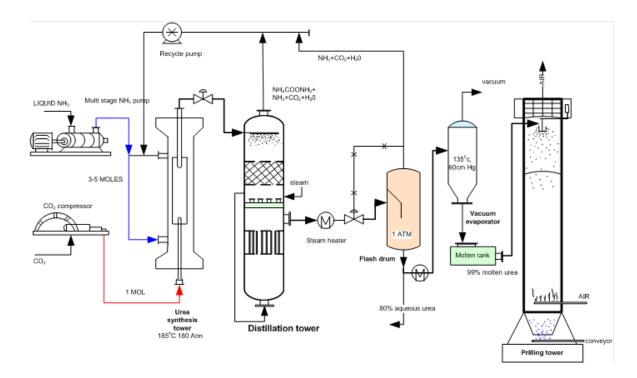


Figure 3.5 Process Flow Diagram of Urea Plant

Figure 3.5 shows the block flow diagram of Urea Plant.

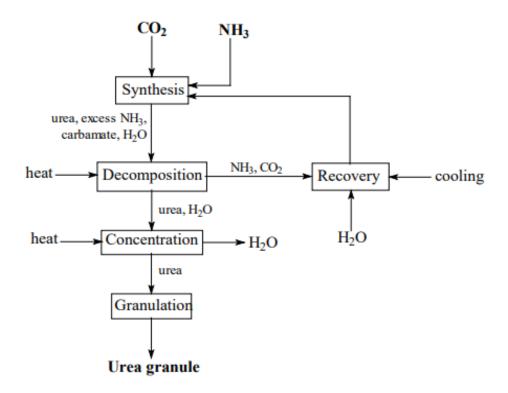


Figure 3.6 Block Flow Diagram of Urea Plant

1) Urea Synthesis

Ammonia (NH3) and carbon dioxide (CO_2) is fed through a pump and compressor respectively into the Urea Synthesis Reactor (See Figure 5.5). A mixture of compressed CO_2 and NH_3 is reacted to form ammonium carbamate in the Urea synthesis reactor.

2) Decomposition / Urea Purification

Water is the most abundant impurity in urea is, followed by unreacted ammonia, carbon dioxide and ammonium carbamate.

Urea purification occurs are called decomposers. In these unit, the ammonium carbamate will be decomposed to ammonia and carbon dioxide. At the same time, some of carbon dioxide and ammonia flash off. A solution of urea dissolved in water and free of other impurities.

Volume 2 Petrochemical Technology

4) Urea Concentration

The urea solution (75%wt) is heated under vacuum, which evaporates off some of the water. Thus, increasing the urea concentration (99%wt) before is sent to the granulation unit.

5) Condensate Treatment

The condensate from vacuum evaporate containing ammonia, carbon dioxide and urea is treated to ensure it's free of contaminant.

6) Granulation / Prilling Tower

All the moisture is removed as the urea form into the granules or in prilled form in granulator or prilling tower.

Application of Ammonia and Urea

Ammonia

- Production of fertilizer.
- Material to prevent freezing of natural latex and synthetic latex.
- Additive such as monosodium glutamate.

Urea

- Fertilizer.
- Used in the preparation of urea formaldehyde resins. These synthetic resins are
 used in the manufacture of adhesive, moulding powders varnishes and melamine
 resins and foams.

3.4 Methanol Plant

Methanol, also known as methyl alcohol, wood alcohol, wood naphtha or wood spirits, has the chemical formula CH3OH (often abbreviated MeOH). It is the simplest alcohol, light, volatile, colourless, flammable liquid with a distinctive odour similar to ethanol (drinking alcohol) but is highly toxic, especially if ingested. The properties of methanol are shown in Table 3.8 below:

Table 3.8 Properties of Methanol

Characteristic Information		
Chemical Name	Methanol	
Chemical Formula	CH₃OH	
Chemical Structure	H-C-O-H H	
Molecular Weight	32.042 kg/kmol	
Boiling Point	65°C	
Freezing Point	-98°C	
Density	791 kg/m³ at 20°C	

Methanol Plant in Malaysia are owned by:

- a) Petronas Chemical Methanol Labuan, Sdn. Bhd (PC Methanol), which is located at Federal Territory of Labuan. There are two plants, PC Methanol 1 which can produce 700 000 tonnes per year of methanol, while PC Methanol 2 can produce 1 700 000 tonnes/year of methanol.
- b) Petronas Chemical Fertiliser (Kedah) Sdn. Bhd (PCFK) Located at Gurun Kedah. This Plant can produce 70 000 tonnes per year of methanol.
- c) The new methanol plant, Sarawak Petrochemical Sdn. Bhd (Sarawak Petchem) which will be located at Bintulu Sarawak expected to operate in 2022. This plant will produce 5 000 tons of methanol per day.

Volume 2 Petrochemical Technology

The Methanol Production Process

Methanol is produced from natural gas (methane). Several technology providers license the process technology for methanol such as:

- Lurgi (used in Petronas Chemical Methanol Labuan and Sarawak Petchem).
- Haldor Topsoe (used in Petronas Chemical Fertiliser Kedah).
- Synetix
- Mitsubishi Chemicals
- KBR

Here we will focus on Lurgi technology which being used by Petronas Chemical Methanol. Lurgi technology is the most technology used in Methanol Plant in the world. For a methanol plant, there are three main section to produce methanol: -

- a) Synthesis Gas (Syngas) Production to reform natural gas to syngas.
- b) Methanol Synthesis to convert syngas to raw methanol.
- c) Methanol distillation to separate raw methanol to get purified methanol.

The reactions of methanol production are as follows:

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CH4 (methane) + H2O = 3H2 + CO
2H2 + CO = CH3OH (methanol)
```

Figure 3.7 shows the block diagram of methanol production process.

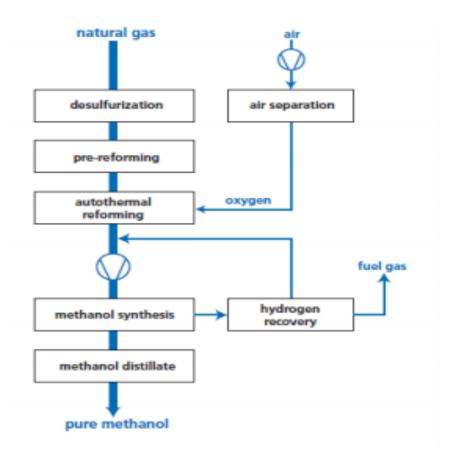


Figure 3.7 Block Diagram of Methanol Plant

1) Synthesis Gas (Syngas) Production

Natural gas is the feedstock for a methanol plant. The first step in methanol production in syngas production. Natural gas was preheated in heat exchanger before entering desulfurizer.

a) Desulfurization

This unit is to remove sulphur because it can lower the catalyst activity and also to protect reformer ad synthesis catalyst from sulphur poisoning. Sulphur is removed by zinc oxide catalyst Reaction occur in this unit are:-

$$H_2S + ZnO \longrightarrow ZnS + H_2O$$

b) Pre Reforming

It is to avoid catalyst coking if the feedstock contain fraction of higher hydrocarbon. The reaction occur in this pre reformer are :-

$$CO + 3H_2 < ----> CH_4 + H_2O$$

Carbon Hydrogen

Methane Water

Monoxide

$$CO + H_2O < ----> CO_2 + H_2$$

Carbon Water

Carbon Dioxide Hydrogen

Monoxide

c) Steam Reformer

Natural gas is combined with steam under heat pressure to produce synthesis gas (syngas) in fired steam reformer. Syngas is a fuel gas consist of hydrogen, carbon monoxide and carbon dioxide.

The reaction on reformer are :-

$$CH_4 + H_2O < ----> CO + 3H_2$$

Methane Water Carbon Monoxide Hydrogen

$$CO + H_2O < ----> CO_2 + H_2$$

Carbon Water

Carbon Dioxide Hydrogen

Monoxide

d) Auto Thermal Reforming

Auto Thermal Reforming used nickel catalyst to reform natural gas to syngas in the presence of oxygen. Pure auto thermal reforming can be used to make syngas whenever light natural gas is available as feedstock. The natural gas (methane) will break down to carbon and hydrogen as below:-

$$CH_4 + 2O_2 < ----> CO_2 + 2H_2O$$

Methane Oxygen

Carbon Dioxide Water

Syngas leaving autothermal reformer (ATR) was cooled by waste heat boiler.

2) Methanol Synthesis

Reformed gas (syngas) from reformer is then compressed and routed to the methanol synthesis unit. In this unit, the syngas gas is then heated and reacted with copper based catalyst in the reactor to produce crude methanol. The synthesis for the reaction occurs as follow:-

(heat)+pressure+catalyst

(heat)+pressure+catalyst

Crude methanol is a mixture of methanol water, small amount of water, dissolved gases and traces of by products. In the hydrogen recovery unit, hydrogen is separated from the purge gas and recycled to the syngas loop. The remaining CH₄-rich gas fraction is used as fuel gas. Crude methanol is then sent to distillation system to be purified.

3) Methanol Distillation

After synthesis, crude methanol which is containing water, a small amount of by products as well as dissolved gases undergoes to distillation unit to be purified into high purity methanol.

The crude methanol is purified in a cost saving 2 column or an energy saving 3 column distillation unit. Distillation unit is to remove other products, based on boiling point at two parts of methanol which are top and bottom part. Distillation at a lower boiling point is to remove dissolved gases and other contaminants with low boiling point of the crude methanol. Distillation in a high boiling point was to remove water and contaminants that have high boiling point.

Application of Methanol

Methanol has been used in a variety application, which can be divided into three categories; feedstock for other chemicals, fuel use and other direct uses as solvent; antifreeze, inhibitor or substrate. The derivatives and applications of methanol are summarized in Table 3.9:

Table 3.9 Application of Methanol and It's Derivatives

ruble 3.3 Application of Methaniorana it 3 Derivatives			
Product	Derivatives		Application
	Formaldehyde	 Formalin Glues & Resins Methylenediphenyl Discocynate (MDI) Butanediol Presticides 	 Antibacterial agent, disinfectant, adhesives, renovation & new building activities, automobile production coatings, panel board and wood & furniture industries.
	Acetic Acid	 Vinyl Acetate Monomer Acetic Anhydride Terephtalic Acid Solvent Acetate 	 Textiles, emulsion paints, solvents & coatins, durable output, automobile production and plastic packaging.

Volume 2 Petrochemical Technology

Product	Derivatives		Application
Methanol	Chemicals	 Methyl Methacrylate (MMA) Solvents Methylamines Chloromethane Dimethyl (DME) Olefins 	 Clear plastic sheets, thickeners, propellant & aerosols and chemical intermediates.
	Fuel	 MTBE Fuel Cells Bio Diesel Gasoline Blending Power Generation 	 Gasoline additives, new & environmentally friendly energy resources and power generation.

3.5 Liquefied Natural Gas Plant

Malaysia is the third largest in the world exporter of Liquiefied Natural Gas (LNG). LNG or Liquefied natural gas is gas that has been cooled to -260°F (-160°C) and converts to a liquid state. LNG is mostly methane plus a small percent of ethane, propane and butane, and trace amounts of nitrogen LNG is in liquid form, which is clear, colorless, odourless, non-toxic and non-corrosive. If spilled, the LNG evaporates quickly and disperses.

LNG production process is through the method of cooling natural gas at temperature of -160° known as liquefaction. At the temperature of -160°, methane (gas) is converted into a liquid form. When natural gas is liquefied, there is a 600% reduction in volume.

Liquefied Natural Gas Plant in Malaysia

LNG is produced in Sarawak, at the Bintulu complex, on the island of Borneo. Malaysia started to export LNG in 1983 (MLNG Satu, three trains), followed by MLNG Dua (three trains) in 1995, MLNG Tiga, two trains in 2003 and Petronas LNG Train 9 (PL9SB), with first LNG delivered in 2016. The Bintulu LNG complex comprises nine LNG trains, with capacity totalling 29.3 million metric tonnes per year.

Petronas also has two floating liquefaction plant. Petronas Floating LNG (PFNLG) is a facility that allows for the processing of LNG to be done offshore hundreds of kilometres away from land. PFLNG SATU successfully loaded 10 LNG cargoes in 2019, after its relocation from the Kanowit gas field in Sarawak to the Kebabangan gas field in Sabah. PFNLG SATU has the capacity to produce 1.2 million tonnes of LNG per year and capable to extract natural gas field in water depths up to 200 metres via a flexible subsea pipeline.

The second floating liquefaction plant (PFLNG Dua) started operate in 2020, is capable of reaching gas field in water depths up to 1,500 metres and able to produce 1.5 million

Volume 2 Petrochemical Technology

Table 3.10 LNG Plant in Malaysia (MIDA, 2020)

tonnes of LNG per year. Table 3.10 shows the LNG plant in Malaysia.

No.	LNG Plant Capacity (mtpa)		y (mtpa)
		Train 1:)
1.	Malaysia LNG Sdn Bhd (MLNG Satu)	Train 2:	8.4 million
		Train 3:	,
	Malaysian LNG Dua Sdn Bhd (MLNG Dua)	Train 4:)
2.		Train 5:	9.6 million
		Train 6:	,
3.	Malaysia LNG Tiga Sdn Bhd (MLNG Tiga)	Train 7	3 7.7 million
3.		Train 8	J. 7.7 million
4.	PETRONAS LNG 9 Sdn Bhd (PL9SB)	Train 9	3.6 million
	Sub-Total	29.3	3 million
5.	PETRONAS Floating LNG Satu (PFLNG Satu)	1.2 million	
6.	PETRONAS Floating LNG Satu (PFLNG Dua)	TRONAS Floating LNG Satu (PFLNG Dua) 1.5 million	
	Total	32.0	million

Liquefied Natural Gas Production Process

The feed gas for the LNG Plant in Bintulu is received from wells in the Central Luconia area of South China Sea, located between 125 and 275 km offshore Bintulu. Natural gas is converted to a liquid in a liquefaction plant, or "train". An LNG train performs three main processes shown in Figure 3.8.

1) **Treating**

The natural gas from the gas field contains the impurities that are not desired for the LNG process and need to be pre-treated. The treating section consists of Sulfinol, Dehydration, Mercury Removal and Scrubbing unit.

2) Liquefaction

The function of this is to liquefy the natural gas to LNG. MMLG satu, MNLG dua and MNLG tiga apply the Propane Pre-cooled Mixed Refrigerant (C3-MR) liquefaction concepts where pre-cooling of the Natural Gas (NG) and the Mixed Refrigerant (MR) is done by means of a propane cooling cycle.

3) Storage

The LNG is stored in an LNG storage tank before being exported. Figure 3.8 below shows the block flow diagram of LNG plant

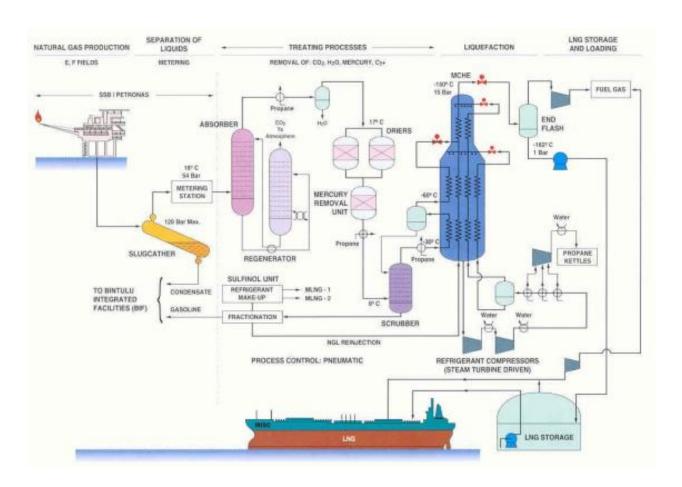


Figure 3.8 Process Flow Diagram LNG Plant

Figure 3.9 shows the Block Flow Diagram of LNG plant.

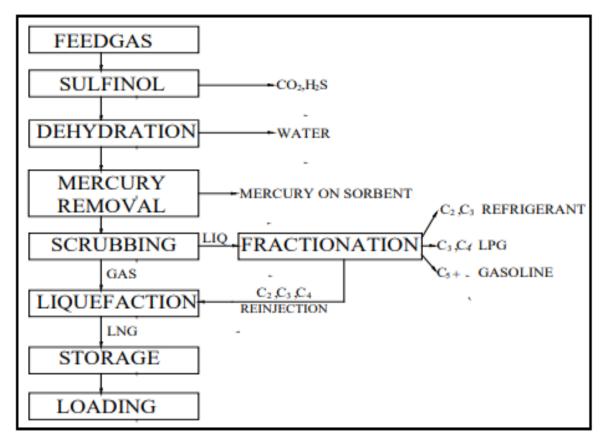


Figure 3.9 Block Flow Diagram LNG Plant

1) Sulfinol Unit.

Natural gas is commonly most made up of methane, however it can include other compounds and gasses such as butane, propane, CO₂ and even oil and water.

This unit is to remove Carbon dioxide (CO₂) and Hydrogen Sulphiede (H₂S) from the raw feed gas. CO₂ needs to be remove for its tendency to form hydrate under very cold operating conditions in liquefaction units. While H2S is removed for its toxicity.

The undesired H2S and CO2 is removed in the Sulfinol Unit by means of absorption with a solvent known as Sulfinol-D and continuously regenerated and stripped of CO₂. As sulfinol contains water, purified gas is saturated with moisture that would freeze out the liquefaction section. Therefore, it must be treated in the Drying Unit.

2) Dehydration Unit

The treated gas from the sulfinol absorber column will be fed into Dehydration Unit.In dehydration unit, water is removed due to its tendency to form hydrates under very cold operating conditions in the liquefaction section. The moisture content is reduced to less than 1 ppm (part per million) by passing the gas through a layer of Molecular Sieves, which are responsible to absorb the water traces from the gas.

3) Mercury Removal Unit

Dried treated gas is then sent into the Mercury Removal unit, to remove the traces of the mercury. The traces of the mercury must be removed to avoid mercury corrosion in Cryogenic Heat Exchanger.

The traces of mercury will react with the impregnated sulphur element from mercury sulphide, which will reside in the mercury removal unit as exhausted adsorbent. This exhausted adsorbent will be changed out every three years. The gas exiting from this unit is considered as treated dry gas ready for the next process.

Scrubber

From the mercury removal unit, the gas is further cooled against high and medium pressure propane and then fed into a Scrubber in which the heavy hydrocarbons will be removed.

Heavy hydrocarbons can be removed by pre-cooling natural gas to 0°C which will partially be condensed in the Scrub Column before the lighter gas phase enters the Main Cryogenic Heat Exchanger (MCHE).

The natural gas components are then fractionated in fractionation units producing methane, ethane, propane and butane. C5+ and heavier components will be sold and exported as gasoline blending.

The extracted methane, and ethane is sent back into liquefaction unit. Propane and butane are sent to the LPG plant in the MNLG terminal to be further refrigerated and exported as LPG to customers.

5) Liquefaction

Main Cryogenic Heat Exchanger (MCHE) is the most important unit of plant-cooling LNG.

Treated gas is then entered into the liquefaction unit using a continuous cooling cycle.

This unit chills and liquefies the gas. Cooling completed in 2 steps:

- 1st: Natural gas are pre-cooled to about the temperature -30°C by propane to remove heat for the subsequent cooling process.
- 2nd: After pre-cooling, natural gas moves through a tube circuit in the main cryogenic heat exchanger (MCHE) where it is liquefied and sub-cooled to between
 -150°C to (-162°C) by mixed refrigerant (MR) flowing down on the shell side.

Before entering the MCHE, The MR is pre-cooled by propane. The vapor and liquid streams pass through separate tube circuits in the MCHE where they are further cooled, liquefied, and sub-cooled.

The two sub-cooled streams are let down in pressure, further reducing their temperatures. As the mixed refrigerant vaporizes and flows downward on the shell side of the MCHE, it provides refrigeration for liquefying and sub-cooling the natural gas.

Finally, LNG pressure is reduced to near atmospheric pressure in the End Flash Vessel to reach the temperature of -160 ° C.

6) Storage

From the liquefaction unit, it is pumped to the LNG storage tank to be stored before export. The storage tank should be able to keep the liquid at low temperature and to avoid evaporation under a stable pressure.

7) Transportation

Tankers equipped with pressurized, refrigerated and insulated tanks are used to transport LNG to the regasification terminal / being exported.

LNG is transported by specialized ships, LNG carriers designed to handle the low temperature of LNG.

Application of Liquefied Natural Gas (LNG)

Malaysia LNG produce is sold to several electric power companies in Japan, Taiwan and South Korea. Products such as liquid propane and butane are used to produce LPG cooking gas for the domestic market and also exported.

3.6 Acrylic Acid Plant

Acrylic acid

Acrylic acid (CH2=CHCOOH) is the simplest unsaturated carboxylic acid. It is a clear, colourless liquid at ambient temperature and pressure. It has a pungent, rancid, irritating, acrid and sweet taste. It is very hazardous when in contact with skin, corrosive to skin and eye contact, skin contact may produce burn, and respiratory tract irritation. The properties of acrylic acid is shown in Table 3.11.

Acrylic acid is produced in only 17 countries in the world. In Malaysia Acrylic Acid Plant located at Gebeng, Pahang owned by BASF Petronas Chemical Sdn Bhd.

Table 3.11 Properties of Acrylic Acid (Wells, 1991)

Characteristic	Information	
Chemical Name	Acrylic Acid	
Chemical Formula	CH2=CHCOOH	
Chemical Structure	H,C,C,O,H	
Molecular Weight	72.06 kg/kmol	
Melting Point	13.5°C at 1 atm	
Boiling Point	141.6°C at 1 atm	
Density	1.051 kg/m³ at 20°C	

Acrylic Acid Processing Plant

Acrylic Acid is produced through a two steps oxidation of propene (propylene) gas with air in the presence of catalysts. After that, acrylic acid is absorbed in a high boiling solvent and then separated from it by distillation.

Propylene (propene) and oxygen are the raw materials required to produce acrylic acid. In addition, catalysts, solvents and molten salts as heat transfer medium are used in the process. Reaction of acrylic acid production are shown below:

Propylene is converted to acrolein

 C_3H_6 (propylene) + O_2 ----- C_3H_4O (acrolein) + H_2O

Acrolein is converted to acrylic acid

 C_3H_4O (acrolein) + $\frac{1}{2}O_2$ ----- $C_3H_4O_2$ (acrylic acid)

Overall reaction are:

 $C_3H_6 + 3/2O_2 - - - C_3H_4O_2 + H_2$

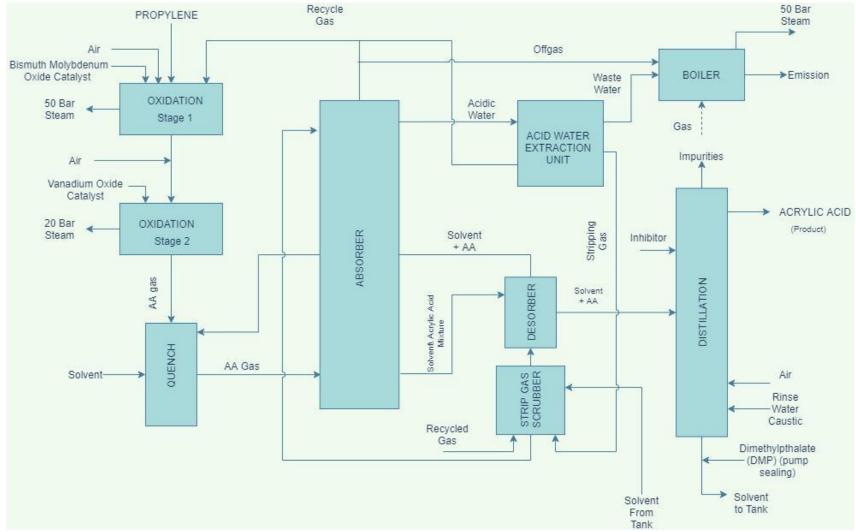


Figure 3.10 Block Flow Diagram of Acrylic Acid Production process (DOE, 2018)

Volume 2 Petrochemical Technology

1) Oxidation

The oxidation process occurs in two stages through a series of two reactors at different temperatures and pressures.

The first stage is the oxidation of propene with air in the presence of Bismuth Molydenum Oxide catalysts in exothermic conditions at a temperature in range 320°C to form acrolein and it's intermediate product.

$$C_3H_6$$
 (propene) + O_2 ----- C_3H_4O (acrolein) + H_2O

The second stage of oxidation, acrolein gas will surpass Vanadium Oxide catalyst also in exothermic at a temperature of about 240 – 300°C to produce acrylic acid.

2) Absorption and Desorber

The gas mixture at the outlet of the second reactor contains Acrylic Acid, Nitrogen, Oxygen, CO, CO₂, un-reacted propylene and traces of acrolein, as well as propane. The hot gas is quenched to approximately 154°C at the Gas Cooler.

It is then fed into Absorption Tower where a high boiling solvent is used to absorb Acrylic Acid.

From the upper section of the absorber, liquid fraction consists of water and some acetic acid is fed to an acid water extraction unit, to recover acrylic acid and then sent to the boiler for incineration.

From the lower section of the absorber, the mixture of solvent and acrylic acid is sent to the Desorber. In this unit, acetic acid, water and acrolein are removed by using stripping gas from the strip gas scrubber.

3) Purification / Distillation

Acrylic acid rich solvent is then fed to distillation in the distillation tower, acrylic acid is separated from the solvent. An inhibitor is added to minimize the formation of polymers. Then, the acrylic acid product is drawn from the side of the distillation tower.

4) Storage

From the distillation tower, acrylic acid is sent to the tank for storage at about 24°C.

Application of Acrylic Acid

According to Table 3.12, there are wider applications of acrylic in petrochemical processing plants such as acrylic monomers use to prepare composite products in industries.

Table 3.12: Application of Acrylic Monomers (BASF-PETRONAS, 2021)

Category	Product Range	Applications	
	Glacial Acrylic Acid	 Disposable diapers, feminine hygiene and adult incontinence products Cable industry of packing industry for medical treatment Floor cleaners and treatment of waste. Fire protection and sealing materials. 	
Acrylic	Butyl Acrylate	 Dispersants, inhibitors and surfactant. 	
Monomers	2 Ethyl Hexyl Acrylate	 Flocculants, dispersants anti scalant Acrylates binders, sizing agents, finishing auxiliaries, leather tanning and leather treatment Adhesives Industrial coatings and agricultural coatings Non-woven fabric Graphic paper 	

Activity 3.0 Review Questions

- 1. State the feedstock used in MTBE Plant.
- 2. Write the structural formula of MTBE.
- 3. State the function of methanol recovery in the MTBE plant.
- 4. Describe the function of Quench Tower in Ethylene Plant
- 5. State the function of polymerisation in Polyethylene Plant.
- 6. State three types of polyethylene produced from a polyethylene plant.
- 7. State two properties of urea.
- 8. Write the balanced equation to produce urea carbamate and urea.
- 9. List two applications of ammonia.
- 10. Explain the process of carbon dioxide removal in an ammonia plant.
- 11. Sketch block diagram with complete labelling depicting processes involved in producing methanol.
- 12. State three main uses of methanol.
- 13. Name two methanol plants in Malaysia.
- 14. Sketch block flow diagram of Liquefied Natural Gas (LNG).
- 15. Why does the temperature of -160° be needed to produce LNG?
- 16. What is the dehydration unit in an LNG plant?
- 17. State the feedstock used in Acrylic Acid Plant.
- 18. Write the reaction equation of acrylic acid production,
- 19. List two applications of acrylic acid.

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