Modelling and Optimization of Sequencing of Processes for Ethylene Production

by

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Dissertation submitted in partial fulfilment of the requirements for the
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved by,

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May 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(NIK ALIFF SYAZREEN BIN SABRI)

ABSTRACT

The separation process for distillation column involves handling a various multi-component mixtures. Particularly for ethylene production, we deal with a number of hydrocarbon components. The objective of this project is to separate each of these components at minimum cost without compromising the feasibility. We develop a superstructure model to determine the optimal design of distillation sequencing for ethylene production. The optimization model is formulated based on a process flowsheet superstructure representation that embeds many possible and feasible structural alternatives for the sequences of processing a multicomponent hydrocarbon mixture constituting liquid naphtha or gaseous ethane. The compositions of the feed will determine the split fractions of the components. We adopt linear mass balance reactor models for conversion of materials into desirable products and simple sharp and non-sharp separation for distillation column. Then, we will formulate a mixed-integer linear program (MILP) that involves two types of variables: (1) discrete 0–1 binary variables for selecting the tasks for an economically-optimal configuration, and (2) continuous variables for determining the optimal operating levels of flowrates into each selected tasks. Using a mathematical modelling, we compare two different feedstocks; liquid naphtha and gaseous ethane. The goal is to select a configuration of separation tasks and their corresponding units. The simulation of our model suggests a different optimal separation sequence from the typical industrial configuration due to the reconditioning of the logical and switching constraints. A more rigorous constraints that consider cost raw material cost, capital investment, production cost and profitability for the olefin production process in order to justify the feasibility of the olefin production is recommended to produce a more reliable output.

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ABBREVIATIONS AND NOMENCLATURE

Sets and Indices

T	Task in a distillation column or reactor
U	Equipment (distillation column or reactor) associated with tasks
S	Set of intermediate products (or streams or components)
pm(T,S)	set maps a task to its intermediate product streams (streams produced by a task)
fm(T,S)	set maps a task to the intermediate product streams that feed the task (materials streams directed to a column)
task_producing_IP(T,S)	set for logical constraints on structural specifications for tasks producing intermediate products (IP)
IP_feed_to_task(T,S)	set for logical constraints on structural specifications connecting a feed stream to a task
outlet_column(T,S)	Set of streams leaving a column

Parameters

TOTFEED	total feed flowrate
spltfrc(T,S)	Split fraction maps unit to intermediate product streams (exclude tasks producing terminal products including component "e")
M(T)	Big M Constant-1000 is the upper bound as it corresponds to the feed flow rate of the intial mixture

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND STUDY

1.1.1 Properties of Ethylene

Ethylene ($H_2C=CH_2$) is a simple naturally occurring organic molecule that is a colorless gas at biological temperatures and also one of the lightest organic component. It is a flammable gas with a slightly sweet smell at normal condition. It is also one of the most versatile and widely used petrochemicals in the world today. Its main use is for the manufacture of polyethylene. In petrochemical industry, ethylene is considered as of the most important olefin hydrocarbons due to its vast array of industrial use.

Mainly, the importance comes from its highly reactive double bond in its chemical structure. This type of bond enables ethylene to undergo all kinds of reactions including addition, oxidation, polymerization and many others, to convert to the final product or intermedial product in the petrochemical engineering industry. In addition, ethylene is also a major raw material to produce plastics, textiles, paper, solvents, dyes, food additives, pesticides and pharmaceuticals. So, the ethylene's use can be extended into the packaging, transportation, construction, surfactants, paints and coatings and other industries.

1.1.2 Ethylene Production

Usually, cracking is widely used in plant to produce ethylene. The process is called pyrolysis or steam cracking. There are also other processes to produce it, like refinery off-gas stream, ethanol dehydration and from coal and coal-based liquids.

Basically, the feedstocks will enter the cracking furnace and mixed with superheated steam. Then it enters the quench tower to some controlled temperature, followed by gas removal and scrubbing. Finally, the pyrolysis gas goes into separation section to be separated into a variety of desired final products.

The increasing worldwide demand for ethylene products has enabled many research and developed processing techniques to increase the yield and minimize the lost. For the production of ethylene, the last section that is the separation process is crucial to separate the multi-components mixture and determine the percentage of yields. Thus, in most situations, the optimal synthesis of separation sequences is highly emphasized and elaborated.

In addition, separation processes in the ethylene plant are energy-intensive, especially distillation. However, it is also one of the most challenging synthesis problems in chemical industry because of the complexity and many possible arrangements available to consider.

1.1.3 **Separation Sequence**

To achieve best separation sequences in the design of chemical processes, it requires the identification of best flow sheet structure system that must carry out for a specific task, such as conversion of raw material into a product or separation of a multi component mixture. To accomplish this goal, many alternatives design must be considered.

There are a few methods developed and proposed to find the solutions for these complications, with appropriate approaches for process synthesis. The three most commonly used approaches for determining optimal configurations of a process plant are heuristics methods (Smith, 2005) and (Nadgir & Liu, 1983), evolutionary method and algorithmic method (Rousseau, 1987, p. 211).

In the separation of olefin, it involves handling a feed stream with a number of hydrocarbon components. The objective is to achieve the least energy consumption at minimum cost. In the algorithmic method for sequencing, one of the approach is superstructure optimization (Lee, Logsdon, Foral, & Grossman) for the olefin separation system. Here, a superstructure of the problem is generated that according to (Andrecovich & Westerberg, 1985) “should contain all feasible distillation sequences and all feasible operating conditions for any column within the superstructure”.

The report will cover the mathematical modelling and optimization of the sequence of the ethylene production, which is the selection of the best element with regard to some criteria from a set of available alternatives. Naphtha and ethane will be the focus subject. The choice of feedstock is a compromise of availability, price and yield.

1.2 PROBLEM STATEMENT

Our work addresses the optimal synthesis of separation sequences given the following data:

- composition and total flow rate of feedstock based on product yields from a thermal cracking unit of naphtha and ethane;
- utility cost coefficients,
- product demands,
- availability and maximum capacity of process units.

We wish to determine the following decision variables, which satisfy the criteria of minimum total annual cost:

- continuous variables on flow rates for each stream involving intermediate products and final products; and
- binary (0 – 1) variables on selection of process units;

1.3 OBJECTIVE

Particularly for ethylene production, optimization applied in ethylene plants is related with the feedstock selection and sequencing of equipment. Among the operational objectives would include yield improvement and production maximization. The main objectives of this study are:

- To compare the effect of different feedstock on the optimal design of ethylene production plant.
- To calculate/estimate split fraction for a distillation column to model distribution of components in top and bottom products.
- To solve a Mixed-Integer Linear Programming optimization model on ethylene production plant.

1.4 SCOPE OF STUDY

The research would be covering the formulation of mathematical modelling for optimization of the sequence of the ethylene plant. The modelling is based on Mixed-Integer Linear Programming which is the mathematical optimization or feasibility program that involves problems in which only some of the variables are constrained to be integers, while other variables are allowed to be non-integers. Using typical feedstock such as naphtha and ethane, we aim to decide continuous variables on flow rates for each stream involving intermediate products and final products and binary (0 – 1) variables on selection of process units which satisfy the criteria of minimum total annual cost. The optimization will also highlight the outcome of various feedstock for ethylene production. For the modelling process, GAMS software will be used to assist the mathematic calculation for optimization as an alternative for EXCEL software.

CHAPTER 2:

LITERATURE REVIEW

2.1 ETHYLENE PROPERTIES

Analysis conducted in a case study reported in (Siemens AG, 2007) states that ethylene is the largest volumes industrially produced organic material and is projected to increase for the near future. Ethylene is one of the basic organic chemicals serving as feedstock for a number of downstream chemical products. With a production exceeding 140 million tons per year, ethylene is by far the largest bulk chemical (in volume) used for the production of around half of all plastics. The demand for ethylene is expected to continue to rise, particularly in the emerging economies.

According to (Saltveit), ethylene is biologically active at very low concentration measured in the ppm and ppb range. Ethylene (C2H4) is a simple naturally occurring organic molecule that is a colorless gas at biological temperatures. About three quarters of atmospheric ethylene originates from natural sources, while one quarter is from anthropogenic sources. The main anthropogenic release is from burning of hydrocarbons and biomass.

“A typical modern plant produces in excess of 800000 t/year.” (Siemens AG, 2007). Feedstock to ethylene plants ranges from light Ethane/Propane mix to heavy naphtha and vacuum gas oils. Most plants are designed with raw material flexibility in mind. Majority of ethylene produced is used in the production of polymers and ethylene derivatives such as ethylene oxide and glycol. A typical ethylene plant also makes a number of other important chemicals such as propylene, butadiene and pyrolysis gasoline. In the past years, ethylene plants have evolved into highly integrated, highly flexible processing systems that can profitably adjust to changing raw material availability and market demands for olefins products. Advanced process control technologies are used in olefins plants, have greatly improved products quality, plant efficiency, and resulted in quick payback of the investment.

Ethylene is a platform petrochemical for direct or indirect production of most important synthetic polymers, including high- and low-density polyethylene (HDPE and LDPE), polyvinyl chloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET) (Shen, Worrell, & Patel, Present and Future Developments in Plastics from Biomass, 2013).

Most studies in the literature related to ethylene production have been conducted to improve the current process technology. Commercially, ethylene is produced by steam cracking techniques and a few choices of feedstock that able to compete in the current market.

2.2 STEAM/THERMAL CRACKING METHOD

Ethylene, because of its double bond, is a highly reactive compound, which is converted to a multi-intermediates and end-products on a large scale industrially. The thermal cracking process is the most interesting process to produce ethylene commercially (Abedi, 2007). This cracking method is applicable for both naphtha and ethane to produce ethylene.

In general, the starting material for ethylene production by steam cracking can be any kind of hydrocarbon. In reality, the choice of starting material is narrowed by economic considerations. The thermal cracking process is fundamentally a dehydrogenation process, accompanied to some extent by polymerization and reactions among products to form the ring structure of aromatics and naphthalene. As the molecular weight of the feedstock increases, the product complexity increases.

The bulk of the worldwide ethylene production is based on thermal cracking with steam. The process is called pyrolysis or steam cracking. (Siemens AG, 2007) states that for the production of light olefins, such as ethylene and propylene, steam cracking is the most useful, and also is the single most energy consuming process in the chemical industry. It is a petrochemical process for producing the lighter alkenes (including ethylene). The saturated hydrocarbons are broken down into smaller, often unsaturated, hydrocarbon and hydrogen.

Having originally been developed in refineries in the United States, steam cracking technology has been around since the 1920s; (heat treatment of crude oil streams was happening previously to enhance the yield of light components) (ChemSystem, 2009).

“Steam cracking globally uses approximately 8% of the sector’s total primary energy use, excluding energy content of final products excluded. In this process, hydrocarbon feedstock, such as naphtha, ethane, etc. are converted to light olefins, such as ethylene and propylene, and other products.” (Siemens AG, 2007). Although it is widely preferred technique, steam-cracking process poses a threat to environment, currently accounts for approximately 180–200 million tons of CO2 emissions worldwide.

Ethylene was formerly produced via ethanol dehydration until 1940’s. With the advent of the economically attractive steam cracking process (Morschbacker, 2009) (Kochar, Merims, & Padia, 1981), almost all ethylene production is now based on various petroleum- based feedstock, including naphtha (mostly in Europe and Asia), ethane and, to a lesser extent, propane and butane in the Middle East and North America. In Western Europe, 95% of ethylene is produced through steam cracking.

With the development of cracking technology, shale gas exploration has opened an opportunity to shift to ethane-based olefins production. In (Foster, 2013), ”The shift from heavier to light feedstocks in the North American olefins markets provides a glimpse of what could happen globally as more countries expand their shale gas efforts.” Although ethane has been long made as feedstock for ethylene plant, it is mainly from fossil fuels, shale gas however, is natural gas and can produce ethane as well.

Based on the available data and current global ethylene production, by 2023, (Gulf Publishing Company, 2013) expects that ethane will replace half of the world’s ethylene feedstock that presently dominated by naphtha. They further compare the growth of ethane demands as feedstock “will expend from 127 million tpy in 2012 to

174 million tpy by 2023, an increase of 47 million tpy. Of this growth, 24 million tons of production will be ethane and LPG based, and 15 million tons will be naphtha-based production."

2.3 SEPARATION/DISTILLATION

For an ethylene plant, the separation system and the refrigeration system are highly integrated. Proper refrigeration scheme is crucial to minimize the cost of production. (Hurstel, Lepetit, & Kaiser, 1981) describes that "a well-organized refrigeration scheme is very important in reducing the plant energy usage." It is very important to sustain the production and cater to market demand.

Optimization of steam cracking technique is important to reduce cost as stated in (Ren, Patel, & Blok, 2006), "Steam cracking globally uses approximately 8% of the sector's total primary energy use, excluding energy content of final products excluded."

According to (Yan, 2000), simulation and optimization work especially for cracking furnace model of the ethylene plant is considered to be established since many pyrolysis yield models have been developed in the last three decades. "The furnace model could be a simple empirical model, a molecular model, or even a mechanistic model."

Design of distillation systems usually comprises of simple columns. Generally, there is a choice of order in which the products are separated that is, the choice of distillation sequence. The sequence is known as the direct sequence in which the lightest component is taken overhead in each column. The indirect sequence, on the other hand, takes the heaviest component as bottom product in each column.

To achieve the best separation process of the cracking system, practically there are a few methods developed for the distillation sequence problem. For a simple non-integrated distillation columns, heuristic have been proposed for the selection. The heuristics are based on observations made in many problems and attempt to generalize the observations. According to (Nadgir & Liu, 1983), heuristic method has taken place to a number of previously used methods. In addition to being restricted to simple columns, the observations apply to heuristics methods are based on no heat integration. Difficulties can arise when the heuristics are in conflict with each other. Fortunately, rather than relying on heuristics that are qualitative and can be in conflict, a quantitative measure of the relative performance of different sequences would be preferred.

On the other hand, evolutionary method suggested in (Rousseau, 1987) seeks to improve the existing flowsheet with elements that describes the evolutionary strategies. In contrast with heuristics, a few additional rules are suggested to be followed. This method also aims to generate a feasible initial sequence. Thus, the initial sequence must be carefully selected with those that are closest to the optimum. Conversely, poor initial choices might possibly lead to failure in choosing the optimal or near optimal sequence. Effective evolutionary methods are important for process synthesis and they may contain either heuristic or algorithmic elements.

Meanwhile, (Andrecovich & Westerberg, 1985), discuss a problem of distillation sequence synthesis that involves heat integration, which is designed as Mixed-Integer Linear Programming (MILP). The method use superstructure optimization. It is an algorithmic method where the use of algorithmic approaches to process synthesis is developed. It will determine the best arrangement of a distillation sequence systematically. This approach starts by setting up a flowsheet that has been embedded with all structural features for an optimal solution. The creation of a superstructure for a distillation sequence and its optimization is straight forward, in principle. Unfortunately, it can be a difficult mixed integer nonlinear programming (MINLP) problem if care is not taken. Such problems should be avoided if possible.

CHAPTER 3:

METHODOLOGY

The research methodology for this project requires the gathering of processing data and available information from company and organization (particularly oil and gas sector) that produce ethylene. The data may include the design flow and capacity, as well as optimization equipment to increase the yield.

3.1 GENERAL PROCESS FOR ETHYLENE PRODUCTION

The most important factor when selecting a process for the ethylene production is the hydrocarbon feedstock.

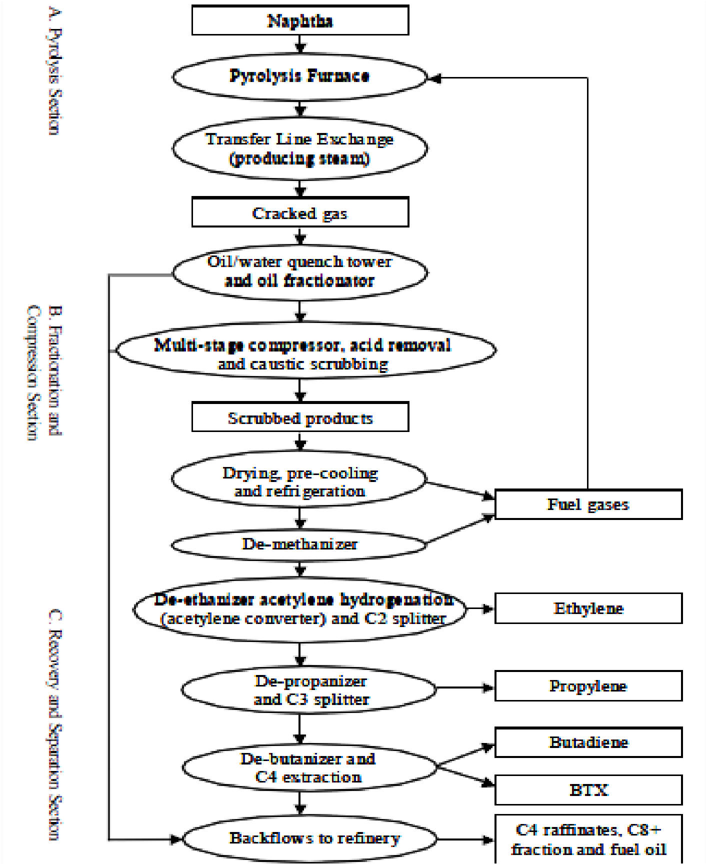


Figure 1 Typical Flow diagram for steam cracking **(Ren, Patel, & Blok, 2006)**

In this report, we will review naphtha and ethane. Although the selection of feedstock is governed by conditions like quantity and quality, studies show that as the molecular weight of the feed hydrocarbon increases, ethylene's yield would also increase. As shown in Figure 1, the ethylene process is comprised of the following three sections: pyrolysis, primary fractionation/compression and product recovery/separation. Overall, ethylene processes for naphtha and ethane requires three similar sections. However, due to feedstock properties and design arrangement, the processes may differ, which often influence fractionation as well as separation sections. As the molecular weight of the feedstock increases, the product complexity also increases.

3.1.1 Pyrolysis Section

The first section of ethylene process is steam cracking. This section produces all the products of the plant, while other sections serve to separate and purify the products. Thus, technically, this section has the greatest effect on the economics of the process. In general, the steam cracking consists of three sections: convection, radiation and transfer line exchanger (TLE). **Figure 2** shows the process diagram of thermal cracking furnace.

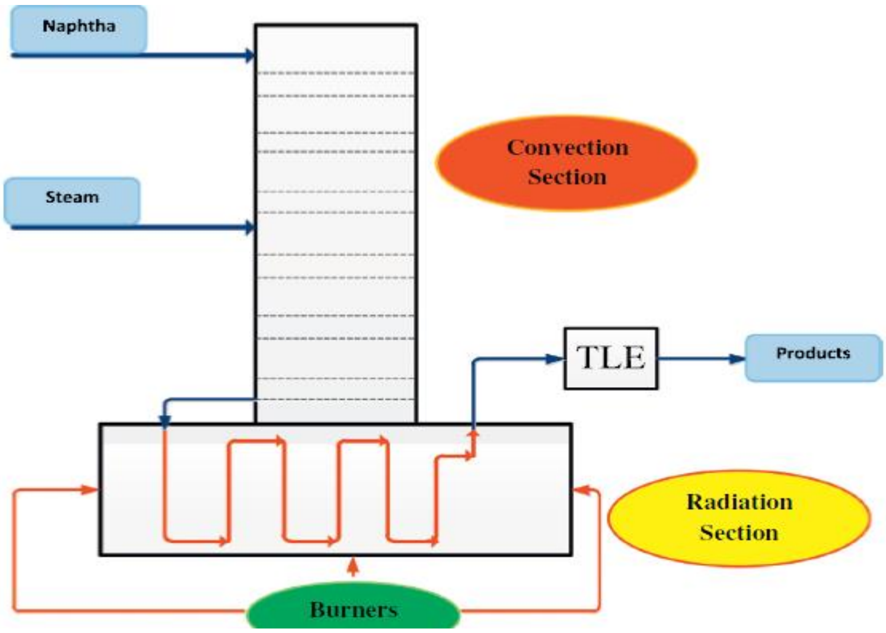


Figure 2: Process diagram of thermal cracking furnace **(Seifzadeh Haghighi, Rahimpour, Raeissi, & Dehghani, 2013)**

Thermal cracking or steam cracking is an endothermic process in which large molecules are broken up into smaller ones. Various types of pyrolysis reactors have been proposed and commercialized for the thermal cracker. In the chemical industry, proper reactor design is crucial because this is where both mixing and reaction occur. There are two types of reactor commonly used in the production of ethylene, which are fired tubular reactor and fluidised bed reactor. We wish to establish a fired tubular reactor (illustrated in **Figure 3**), which consists of the following:

Steam Cracking Furnace

- Receives combined feed and steam to crack feeds into ethylene and various by-products.

The lower hydrocarbons such as ethane and naphtha usually use this reactor by adopting direct heating process. In this reactor, it is importance to ensure that the feedstock does not crack to form coke. In order to avoid the formation of coke, the gaseous feedstock needs to pass very quickly and at very low pressure. The steam is introduced in the process to reduce the partial pressure of hydrocarbon, lower the residence time of the hydrocarbon and decrease the rate of coke formation within the tubes. In the radiant section, the endothermic reaction in the thermal cracker occurs less than a second as the mixture of hydrocarbon passes through the long tubular tubes.

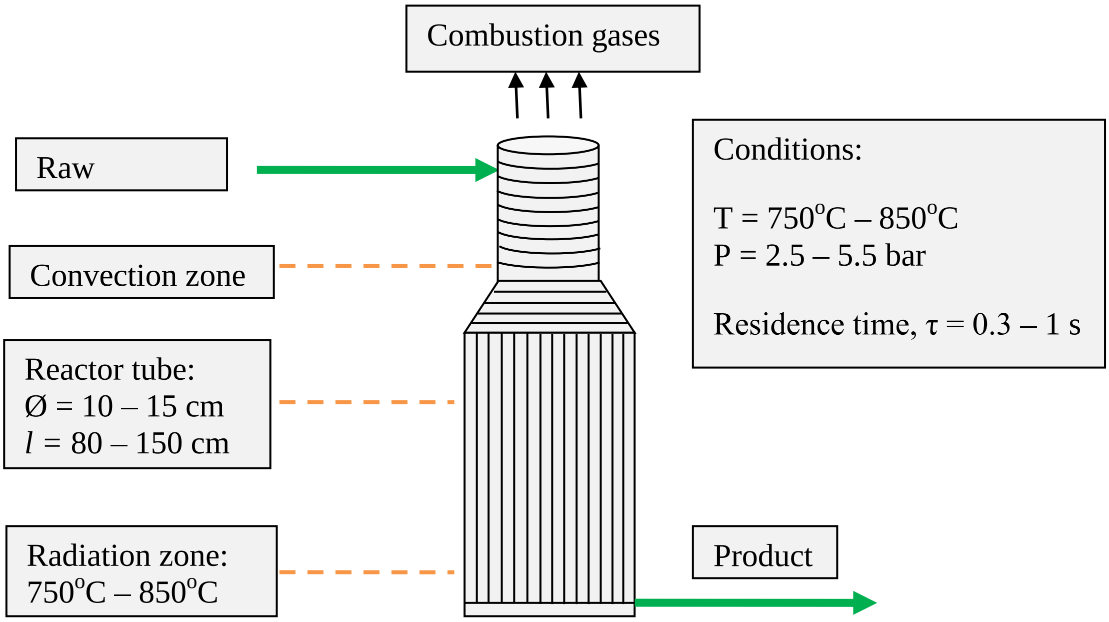


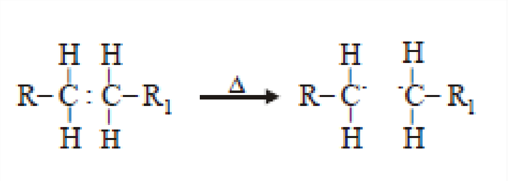
Figure 3: Design considerations for fired tubular tubes reactor **(Jukic, 2013)**

The feed will enter the convection zone at a given temperature and pressure. Then the hydrocarbon will be mixed with steam to reduce its partial pressure and reduce coke formation as well as lower the residence time of the hydrocarbon. The ratio steam to hydrocarbon added is specified to achieve best economic and reaction. In convection section, no cracking reaction occurs. After that, it goes down into radiation section, which is the heart of the reactor, and where cracking reaction takes place in the long tubular tubes. At this point, the feedstock will break up to ethylene, methane, propane, butane, butene, ethane, propadiene, propylene, methane, hydrogen, fuel gas, pyrolysis gasoline, butadiene and other insignificant amount of hydrocarbon.

The pyrolysis is a non-catalysed process of thermal decomposition of hydrocarbon in the production of ethylene. The process needs to be performed at very high temperatures, 750-900^{o}C, at approximately 2-4 bar. Cracking reaction of one or more covalent carbon-carbon bond in hydrocarbon molecules take place by free radical mechanism which leads into a large formation number of smaller molecules. The dehydrogenation process also occurred at the same time.

In thermal decomposition, there are at least three basic reactions by mechanism of free radicals, which are initiation or start of a reaction, propagation or reaction advancement, termination or reaction stop and transfer of chain reaction.

Thermal decomposition by free radical chain mechanism:



Formation of olefin hydrocarbons:

(1) *C−C bond cleavage*

$$CH_3{-}CH_2{-}CH_3 \xrightarrow{\Delta} CH_2{=}CH_2 + CH_4$$

(2) *C−H bond cleavage (dehydrogenation)*

$$CH_3{-}CH_2{-}CH_3 \xrightarrow{\Delta} CH_3{-}CH{=}CH_2 + H_2$$

For the optimization, a higher cracking temperature is preferable to produce higher amount of ethylene (ethene). This is also referred as severity. On the other hand, lower severity will produce higher amount of propylene (propene) and other C4's products. Thus, severity can be used as a constraint in the process and theoretically, it is the purpose of the optimization process.

For feedstock like ethane and propane, the severity of the cracking is directly evaluated by the conversions of the feedstocks, which are defined by the fractional disappearance of the reactants. As for naphtha, the main parameters affecting the product distribution are feed composition, reactor gas temperature, steam ratio and residence time. **Figure 4** shows the conversion of the feedstocks.

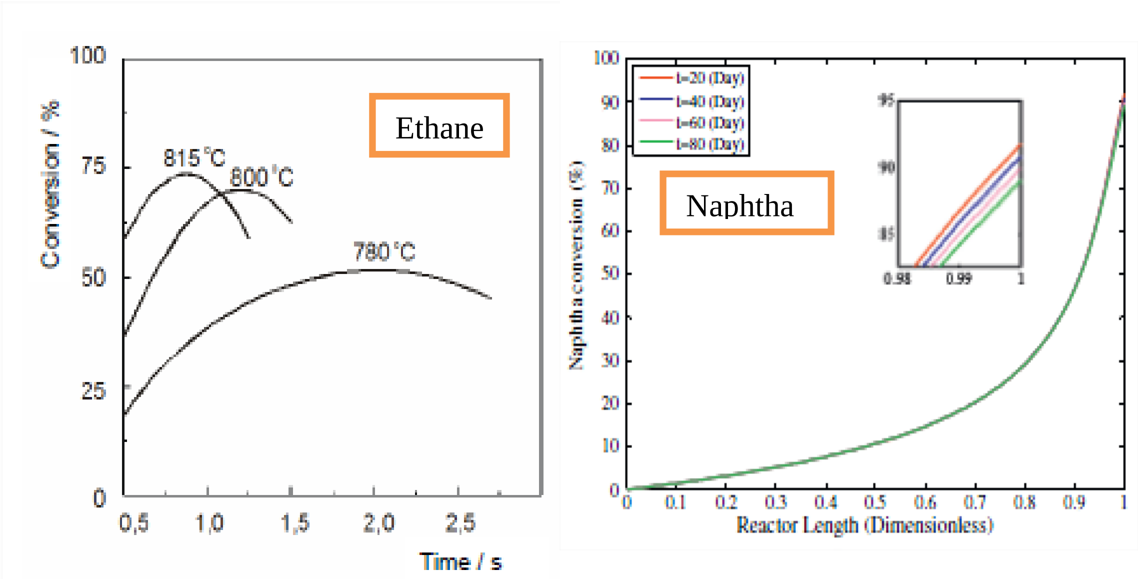


Figure 4: Conversion of ethane, propane and naphtha to ethylene. **(Seifzadeh Haghighi, Rahimpour, Raeissi, & Dehghani, 2013)** and **(Jukic, 2013)**.

3.1.2 Fractionation and Compression Section

After a series of heating, the products leave this section and enter the TLE section. In this part, the product is cooled down to inhibit other side reactions. In gas compression and treatment section, processes like removal of acid gases, drying of cracked gases and purification of ethylene are integrated to produce ethylene with high purity. In most ethylene plant, compression of the pyrolysis gas leaving the quench tower is a high concern. It is important for treating the subsequent cryogenic.

While this liquid fraction is extracted, the gaseous fraction is desuperheated in the quench tower by a circulating oil or water stream.

Consequently, the cooled cracked gas leaving the water tower is compressed in four to five stages. Plants based upon gaseous feedstock generally employ four stages, while many naphtha-and gas oil-based plants employ five stages of pyrolysis gas compression. The caustic scrubber located in the plant aids in removing acid gases such as carbon dioxide and hydrogen sulfide. The compressed cracked gas usually is dried to reduce the moisture content before separation process takes place.

i. Transfer Line Exchanger

Objective:

- To rapidly cool the cracked products to obtain the maximum gain of ethylene.

Equipment Capability:

- Able to cool down and lower the temperature of cracked ethylene and byproducts to as low as 450K.

ii. Quench Tower

Objectives:

- To spray quenching water to further cool down the cracked products.
- To separate gasoline from the cracked ethylene and byproducts.

Operating Conditions:

- Might require new feed of quenching water from time to time to make up the loss of water during quenching.

iii. Dissolved Gas Stripper

Objective:

- To strip dissolved gasses such as acetylene and carbon dioxide.

iv. Compressor

Objective:

- To increase pressure of the cracked ethylene and by-products.

Equipment Capability:

- Able to increase the pressure of cracked ethylene and products up to 3500kPa.

v. Caustic Tower

Objective:

- To remove organic sulfide and acidic compounds through caustic washing.

vi. Water Remover

Objective:

- To remove any remaining water from the cracked ethylene and byproducts.
- Drying is by using silicon oxide as the absorber.

3.1.3 Recovery and Separation Section

After quenching process, compression and acid gases removal, and finally drying, the cracked gas will then undergo the separation process. At this stage, the product generally contains hydrogen and light hydrocarbons in the C_1-C_6 range.

Table 1: Typical yields of feedstocks in olefin production

	Feedstocks			
	Ethane (wt %)	Propane (wt %)	Naphtha (wt %)	Gas Oil (wt %)
H_2	3.6	1.3	0.8	0.6
CH_4	4.2	24.7	15.3	10.6
C_2H_2	0.2	0.3	0.7	0.4
C_2H_4	**48.2**	**34.5**	**29.3**	**24.0**
C_2H_6	40.0	4.4	3.8	3.2
C_3H_4	1.3	0.3	1.1	1.0
C_3H_6		14.0	14.1	14.5
C_3H_8		10.0	0.3	0.4
1.3-C_4H_6	1.6	3.7	4.8	4.7
C_4H_8			4.2	4.5
C_4H_{10}			0.3	0.1
Pyrolysis Gasoline	0.9	5.9	21.0	18.4
Fuel Oil	**-**	0.9	3.8	17.6

For this separation, several columns will be used to separate multi-component mixtures into pure or multi-component product streams. **Table 1** shows the yields of feedstocks in olefin production. Thus, there is a substantial economic incentive in selecting the best separation column sequence for a particular separation.

Based on literature and current ethylene plant processing worldwide, we have made a general diagram that exhibits the main process at the plant. This sequencing is applicable for different feedstock (naphtha and ethane) with some minor adjustments for optimization. The sequencing of distillation column is based on the literature to get the best yield for our ethylene plant.

A simplified process flow diagram is developed to understand the overall processing plant of ethylene. **Figure 5** illustrates the general sequencing of ethylene plant that will assist to help understanding the major process at the plant.

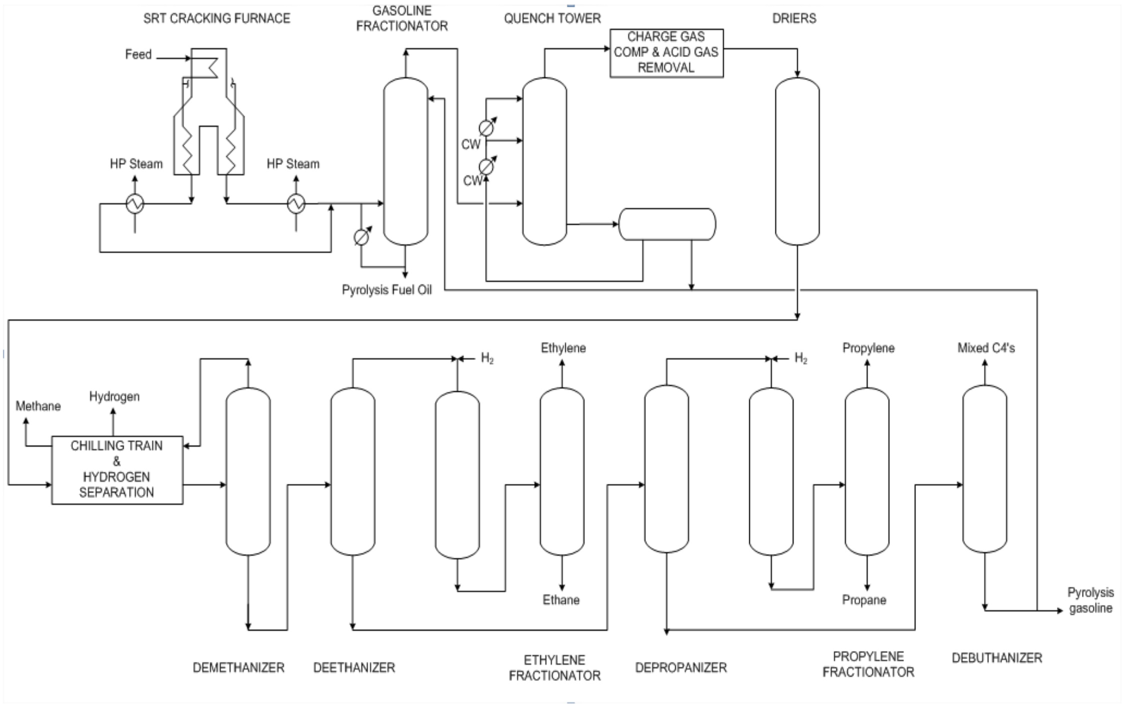


Figure 5: General Sequencing Ethylene Plant for Steam Cracking Process

The essential part of product recovery/fractionation is when separation process takes place through distillation, refrigeration and extraction. Separation process (especially distillation) is very energy-intensive and it amounts to the total capital investment and operating costs involved in a chemical plant. We will consider all columns involve in the distillation perform sharp-separation except for de-propanizer. The equipment involve in the separation process through distillation, refrigeration, and extraction are as follow:

i. Depropanizer

Objective:

- To separate propane and propylene at the top column as a distillate.

There are two possibilities of separation that will be considered for depropanizer:

1- Sharp-separation;
2- Non-sharp separation.

The dried gases are cooled and fed to the HP depropanizer, which separates the feed into an overhead vapor and a bottoms product. LP depropanizer produces a raw C3 (hydrocarbon with three carbon atoms) liquid distillate which is sent to C3 hydrogenation and a bottom stream which flows to the Debutanizer.

ii. Acetylene Removal

Acetylene is produced as an impurity in the ethylene cracking heaters and so, must be converted to increase the yield of ethylene. Acetylene converter is to hydrogenate acetylene compound and to convert it into ethylene. Gas from the fifth stage of the cracked gas compressor is catalytically hydrogenated to remove acetylene. Essentially, all acetylene is converted to ethylene and ethane. Dried gas is cooled and partially condensed to provide reflux for the hp depropanizer.

iii. Demethanizer

It is designed to completely separate methane from ethylene and heavier components. The overhead consists of methane and some impurities of hydrogen. The prefractionator separates C3 and heavier material from C2 and lighter. The overhead vapor from the prefractionator, which contains essentially no C3 material, is sent to the demethanizer. The prefractionator bottom is sent to the deethanizer.

vii. Deethanizer

There are also two possibilities of separation that will be considered for debutanizer:

1. Sharp-separation;
2. Non-sharp separation.

The deethanizer separates C2 hydrocarbons as overhead (acetylene, ethane and ethylene) and C3 and heavier hydrocarbon as bottoms. The C2 splitter is a single tower operated at low pressure and temperature. Two feeds enter the tower; an ethylene rich vapor stream from the demethanizer and the overhead liquid product from the deethanizer.

viii. Ethylene Fractionator (C2 Splitter)

After acetylene removal, the dried gas enters the ethylene fractionator to separate ethane and ethylene. The ethylene produced is our yield while the ethane will be recycled to cracking furnaces. The C2 splitter makes a sharp separation between ethylene and ethane. The ethylene product is pumped to high pressure, heated, and delivered to storage as a vapor product. If required, approximately 70% of the nameplate ethylene production can be subcooled and sent out entirely as a liquid product.

iv. C3 hydrogenation

Raw C3 from the deethanizer bottom and LP depropanizer overhead are catalytically hydrogenated to remove methylacetylene and propadiene. Methylacetylene and propadiene are converted to propylene.

v. C3 splitter or Propylene Fractionator

The overhead of the DePropanizer is sent to the propylene fractionator (C3 splitter) for further processing. The net bottom liquid is recycled back to the LP depropanizer to remove any green oil produced in the C3 hydrogenation unit.

vi. Debutanizers Systems

The bottom of depropanizer is further processed here. The debutanizer receives a liquid feed from the LP depropanizer bottom. A separation is made between C4 and C5 (hydrocarbon with five carbon. The net overhead product is sent to the C4 hydrogenation unit and the bottom is combined with the distillate stripper bottom, cooled and sent to the pyrolysis gasoline hydrogenation unit.

vii. C4 and Pyrolysis

The C4 hydrogenation unit selectively converts butadiene to butenes using high purity hydrogen. The unit consists of a single fixed-bed catalytic reaction system. The C4 product stream is recycle cracked in the cracking furnaces.

viii. Hydrogenation Unit

The pyrolysis gasoline hydrogenation unit is a one-stage catalytic reaction system to selectively hydrogenate diolefins and styrenic compounds. A stabilizer removes dissolved lights and a rerun tower removes gums from the gasoline product.

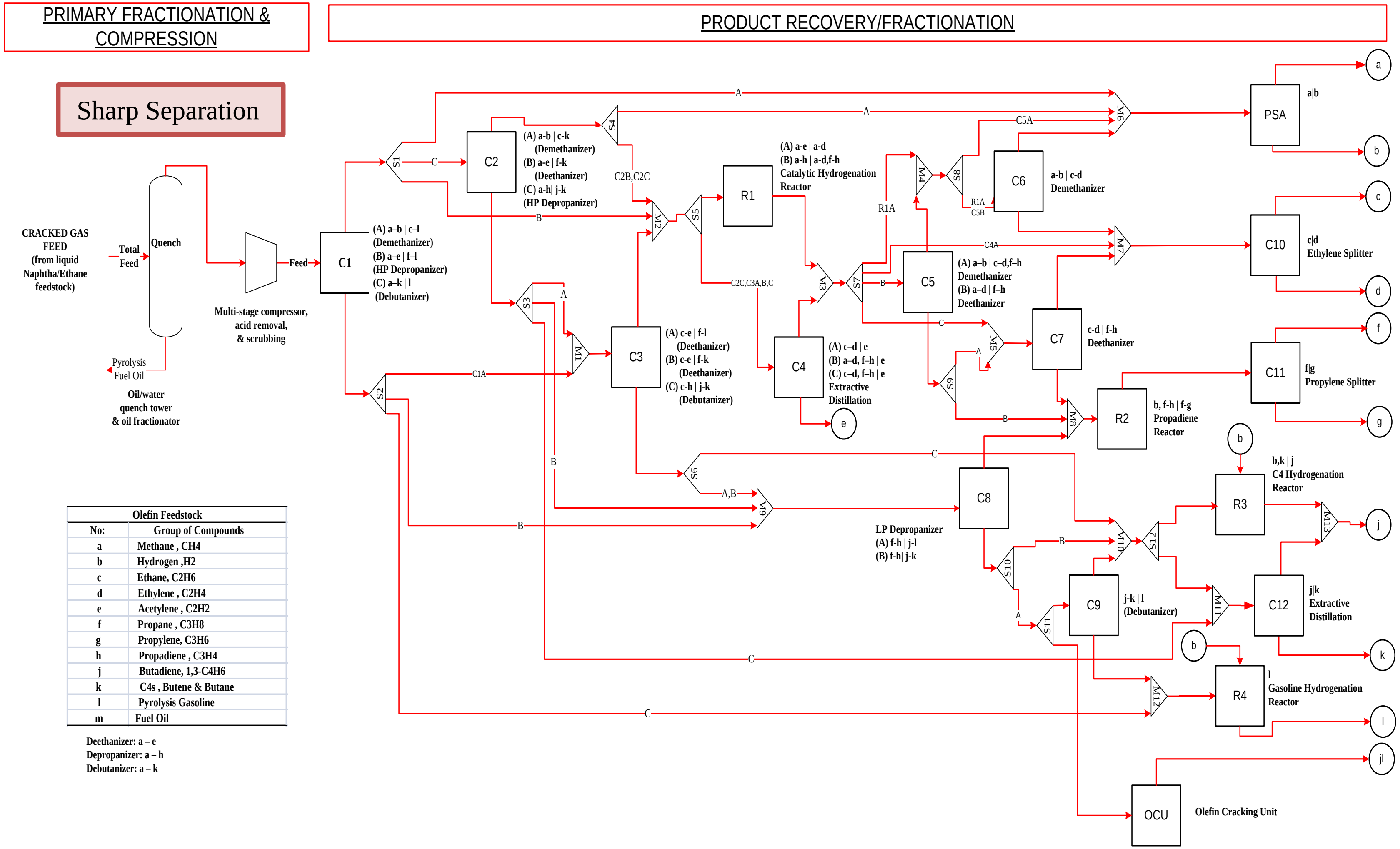
ix. Olefin Cracking Process

Olefin cracking process converts C_4 to C_8 olefins to propylene and ethylene at high propylene and ethylene ratio.

3.2 SUPERSTRUCTURE REPRESENTATION

As highlighted in literature, we will perform superstructure representation for our optimization model formulation. The superstructure was developed to include all possible separation sequences for olefins. It consists of many possible alternatives to produce ethylene.

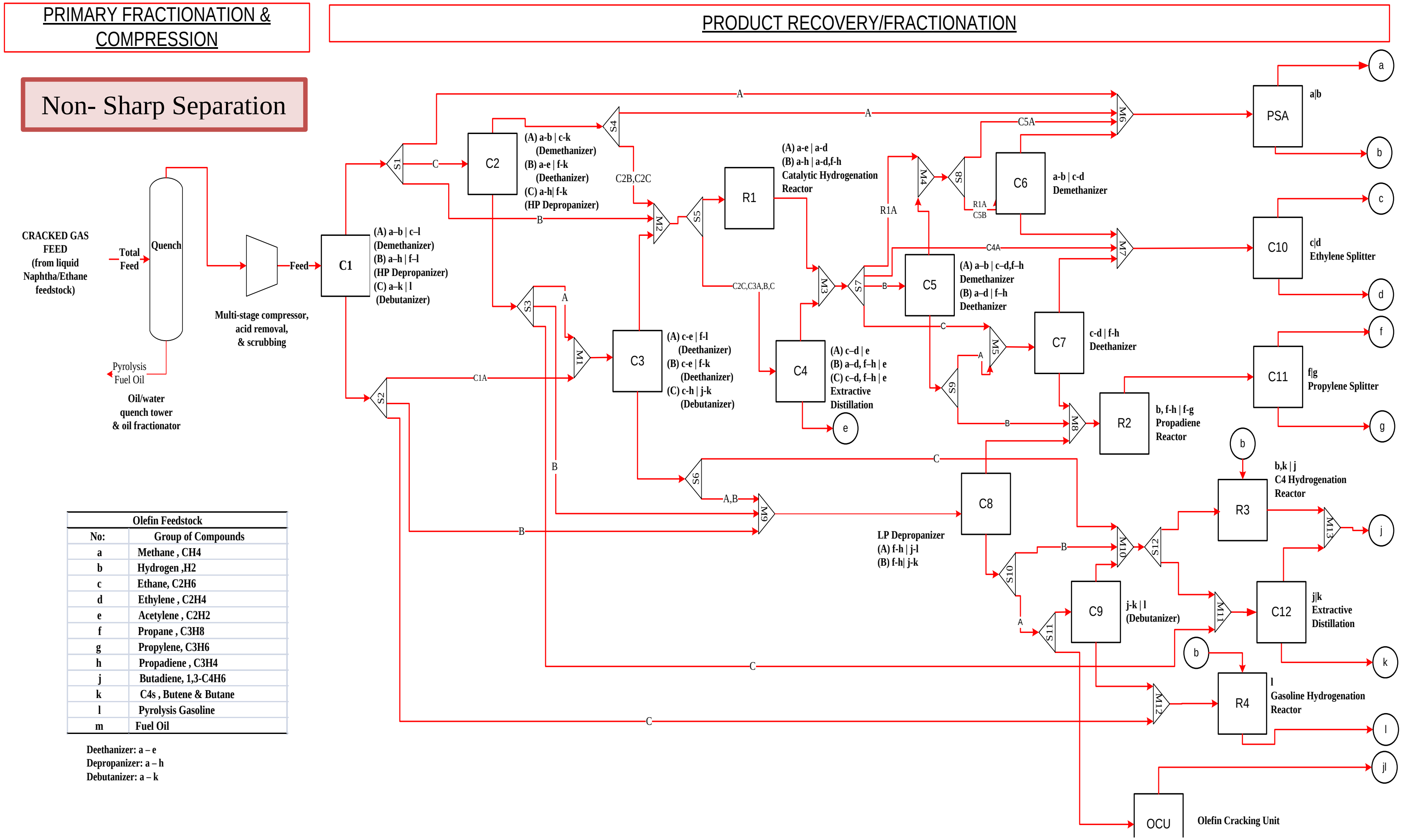
According to (Andrecovich & Westerberg, 1985) a superstructure of distillation columns is constructed from single distillation tasks. These single tasks can be combined to form distillation sequences and the sequences can be combined to form a superstructure. Describing the distillation tasks and sequences, which can be used for a given problem, is easy if only simple, sharp distillation columns are used and if only pure products are desired. We will consider superstructure for sharp and non-sharp separation as illustrated in Figure 6 and **Figure 7** respectively.



Olefin Feedstock	
No:	Group of Compounds
a	Methane , CH4
b	Hydrogen ,H2
c	Ethane, C2H6
d	Ethylene , C2H4
e	Acetylene , C2H2
f	Propane , C3H8
g	Propylene, C3H6
h	Propadiene , C3H4
j	Butadiene, 1,3-C4H6
k	C4s , Butene & Butane
l	Pyrolysis Gasoline
m	Fuel Oil

Deethanizer: a – e
Depropanizer: a – h
Debutanizer: a – k

Figure 6: Superstructure representation for the separation of olefins from naphtha and ethane for sharp separation.



Olefin Feedstock	
No:	Group of Compounds
a	Methane , CH4
b	Hydrogen ,H2
c	Ethane, C2H6
d	Ethylene , C2H4
e	Acetylene , C2H2
f	Propane , C3H8
g	Propylene, C3H6
h	Propadiene , C3H4
j	Butadiene, 1,3-C4H6
k	C4s , Butene & Butane
l	Pyrolysis Gasoline
m	Fuel Oil

Deethanizer: a – e
Depropanizer: a – h
Debutanizer: a – k

Figure 7: Superstructure representation for the separation of olefins from naphtha and ethane for non-sharp separation.

It is still necessary to specify the number of columns performing each distillation task after connecting distillation and their sequences. The objective function of superstructure is based on the yield of reactions.

In general, the mathematical programming approach to process synthesis and design activities and problems consists of the following four major steps (Floudas, 1987) (Grossman, Caballero, & Yeomans, 1999) as shown in Figure 8.

1. Development of the superstructure to represent the space of topological alternatives of the naphtha flow to petrochemical plant configuration;
2. Establishment of the general solution strategy to determine the optimal topology from the superstructure representation of candidates;
    - If model is largely linear, simultaneous solution strategy is used.
    - If model is non-linear, sequential solution strategy is used (1st stage, solve NLP (fix binary variables), 2nd stage, solve MILP (NLP solution).
3. Formulation or modelling of the postulated superstructure in a mathematical form that involves discrete and continuous variables for the selection of the configuration and operating levels, respectively; and
4. Solution of the corresponding mathematical form, i.e., the optimization model from which the optimal topology is determined.

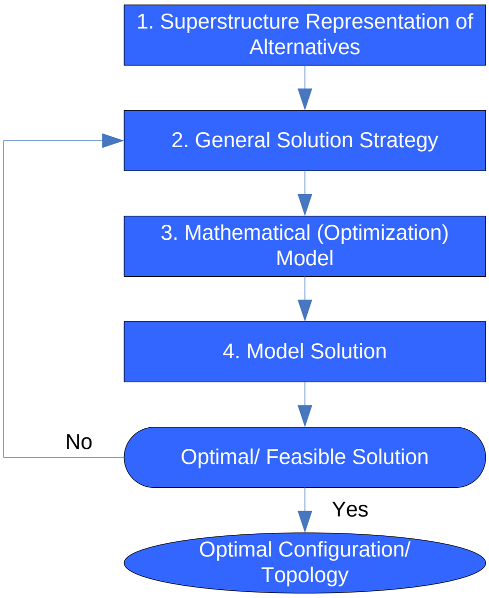


Figure 8: Steps in mathematical programming approach to process synthesis and design problems

3.3 COMPOSITION MODELLING

3.3.1 Feedstock Compositions

From the literature, we have analysed a few set of compositions of naphtha and ethane as tabulated in Table 2 and Table 3. For simplicity, we have taken a normalized composition by eliminating negligible and low percentage components.

Table 2: Naphtha composition after cracking

Components	Naphtha A	Naphtha B	Naphtha C	Naphtha D
Methane , CH_4	11.98	15.08	14.22	15.3
Hydrogen ,H_2	0.54	0.71	0.71	0.8
Ethane, C_2H_6	3.97	3.90	3.40	3.8
Ethylene , C_2H_4	19.46	23.24	24.01	29.3
Acetylene , C_2H_2	0.09	0.25	0.28	0.7
Propane , C_3H_8	0.56	0.49	0.45	0.3
Propylene, C_3H_6	16.15	15.96	15.51	14.1
Propadiene , C_3H_4	0.31	0.63	0.68	1.1
Butadiene, 1,3-C_4H_6	3.73	3.90	4.28	4.8
C4s , Butene & Butane	10.56	6.73	7.70	4.5
Pyrolysis Gasoline	30.19	25.73	25.80	21
Fuel Oil	2.46	3.36	2.95	3.8

Table 3: Ethane composition after cracking

Components	Ethane A	Ethane B	Ethane C
Methane , CH_4	3.08	6.21	5.64
Hydrogen ,H_2	3.35	4.21	4.27
Ethane, C_2H_6	46.0	30.93	30.6
Ethylene , C_2H_4	42.5	50.1	51.45
Acetylene , C_2H_2	0.14	0.32	0.38
Propane , C_3H_8	0.16	0.22	0.2
Propylene, C_3H_6	1.41	1.67	1.55
Propadiene , C_3H_4	0.01	0.02	0.02
Butadiene, 1,3-C_4H_6	0.89	1.41	1.47
C4s , Butene & Butane	0.56	0.49	0.47
Pyrolysis Gasoline	1.82	3.94	3.57
Fuel Oil	0.08	0.48	0.38

3.3.2 **Split Fractions**

We have synthesized a split fraction for each component by considering our assumptions earlier. The objective of split fraction method is to analyse the feasibility of the separation in the column by taking reference of calculation from Mixed-Integer Linear Programming (MILP) to solve for split fraction of the components.

For the superstructure developed, we will consider a sharp separation for all columns except for depropanizer in column 1 (C1b) and debutanizer in column 2 (C2c) which have two situations:

- Sharp-separation; which means that all components leaving only in either stream, as distillate or bottom product and there is no overlapping components.
- Non-sharp separation; some of the components will leave the column in two different streams, and will cause overlapping of components.

As stated by (Andrecovich & Westerberg, 1985), material balance constraints relate material flows into and out of columns in the superstructure. Each column separates its feed into two products streams whose amounts are related to the feed flow by:

$$\begin{aligned} D_t &= \xi_D F_t \\ B_t &= \xi_B F_t = (1-\xi_D)F_t \end{aligned} \qquad \textbf{(1)}$$

where ξ_D *is the split fraction of the feed to task t, which leaves in the distillate and* ξ_B *is the split fraction that leaves at the bottom.*

The constraint is written for each product produced by columns in the structure must equal to the amount of that intermediate product fed to columns which further separate the product.

$$\sum_{t\in PS_m} \xi_t F_t - \sum_{t\in FS_m} F_t = 0 \qquad s \in IP \qquad \textbf{(2)}$$

where PS_s *is the set of all columns which produce a given intermediate product s as distillate or bottoms,* FS_s *is the set of all columns having intermediate product s as* *feed, F is the total flow rate to a column, IP is the set of all intermediate products, and ξ is the split fraction relating distillate or bottoms flows to feed flows. This constraint (2) is written for each intermediate product.*

A similar expression is necessary for the feed to the distillation system:

$$\sum_{t \in FS_F} F_t = F_{TOT} \tag{3}$$

Sharp-Separation

For sharp separation, all columns will have no overlapping components. Thus, referring to

Figure 6, we assume;

- Column 1 for depropanizer (C1b) separates a-e and f-l from a-l
- Column 2 for debutanizer (C2c) separates a-h and j-k from a-h

Referring to equation above, the total feed to the system must equal the sum of the feeds to all columns, which will process some portion of the feed stream. In order to reduce the size and complexity of the MILP model for olefin production, there are a few assumptions are made. Below are the assumptions:

- Use linear constant-yield material balances
- 100% recoveries (then for each column, we can determine a priori, the fractions of the total feed that are recovered at the top and at the bottoms)

For each column, the calculation (5) procedure to obtain the split fractions is as shown in Figure 9.

$$\begin{gathered}
\xi_{t,\mathrm{top}} = \frac{\sum\limits_{i \in C_{t,top}} x_{i,\,feed}}{\sum\limits_{i \in C_t} x_i} \\
\xi_{t,bottom} = \frac{\sum\limits_{i \in C_{t,bottom}} x_{i,\,feed}}{\sum\limits_{i \in C_t} x_i}
\end{gathered} \tag{4}$$

where; $x_{i,\,feed}$ *= mole fraction of component i in the initial mixture,*

C_t = *set of component in the feed*

$C_{t,top}$ = *set of components in the top or overhead,*

$C_{t,bottom}$ = *set of components in the bottom of column k*

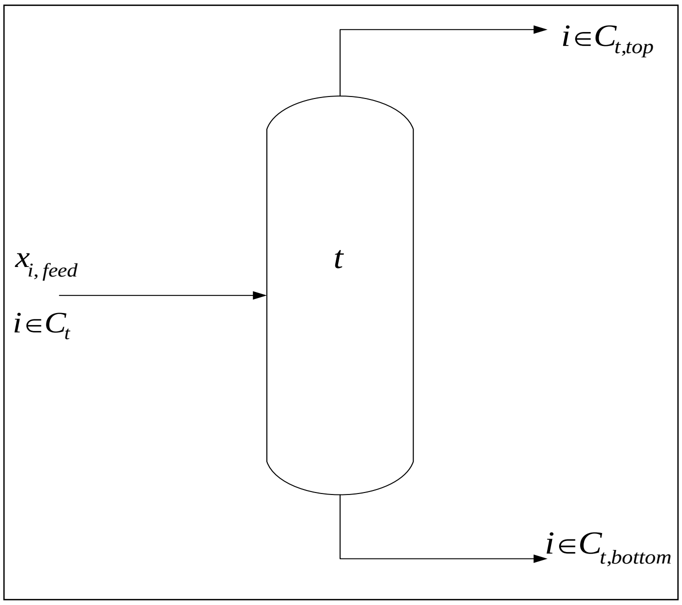


Figure 9 Module for total flow with sharp split

Non-Sharp Separation

For non-sharp separation of multi-components mixture, we will only consider the depropanizer and debutanizer column. In the depropanizer column, there two sets of tasks that have overlapping components. As **Figure 7** implies, for task (B) in column 1 (C1) which is to separate components a-h and f-l from a-l, there are three components (f, g and h) that overlap as outputs.

The same situation occurs in column 2 for debutanizer (C2c) which is to separate a-h and f-k from a-h, components f, g and h are overlapping for both product streams. Consequently, we have developed a general formula to calculate the fractions of the overlapping components.

i. Depropanizer:

(C1b) separates a-h and f-l from a-l.

$$\xi_{\mathrm{C1b}}^{ah} = \frac{\sum_{\alpha=a}^{e} x_{\mathrm{C1b}}^{\alpha} + \frac{1}{4}\sum_{\alpha=f}^{h} x_{\mathrm{C1b}}^{\alpha}}{\sum_{\alpha=a}^{e} x_{\mathrm{C1b}}^{\alpha} + \frac{1}{2}\sum_{\alpha=f}^{h} x_{\mathrm{C1b}}^{\alpha} + \sum_{\alpha=j}^{l} x_{\mathrm{C1b}}^{\alpha}} \qquad \textbf{(5)}$$

$$\xi_{\mathrm{C1b}}^{fl} = \frac{\frac{1}{4}\sum_{\beta=f}^{h} x_{\mathrm{C1b}}^{\beta} + \sum_{\beta=j}^{l} x_{\mathrm{C1b}}^{\beta}}{\sum_{\beta=a}^{e} x_{\mathrm{C1b}}^{\beta} + \frac{1}{2}\sum_{\beta=f}^{h} x_{\mathrm{C1b}}^{\beta} + \sum_{\beta=j}^{l} x_{\mathrm{C1b}}^{\beta}} \qquad \textbf{(6)}$$

ii. Debutanizer:

(C2c) separates a-h and f-k from a-h

$$\xi_{\mathrm{C2c}}^{ah} = \frac{\sum_{\alpha=a}^{e} x_{\mathrm{C2c}}^{\alpha} + \frac{1}{4}\sum_{\alpha=f}^{h} x_{\mathrm{C2c}}^{\alpha}}{\sum_{\alpha=a}^{e} x_{\mathrm{C2c}}^{\alpha} + \frac{1}{2}\sum_{\alpha=f}^{h} x_{\mathrm{C2c}}^{\alpha} + \sum_{\alpha=j}^{l} x_{\mathrm{C2c}}^{\alpha}} \qquad \textbf{(7)}$$

$$\xi_{\mathrm{C2c}}^{fk} = \frac{\frac{1}{4}\sum_{\alpha=f}^{h} x_{\mathrm{C2c}}^{\alpha} + \sum_{\alpha=j}^{k} x_{\mathrm{C2c}}^{\alpha}}{\sum_{\alpha=a}^{e} x_{\mathrm{C2c}}^{\alpha} + \frac{1}{2}\sum_{\alpha=f}^{h} x_{\mathrm{C2c}}^{\alpha} + \sum_{\alpha=j}^{l} x_{\mathrm{C2c}}^{\alpha}} \qquad \textbf{(8)}$$

3.4 Mathematical Programming Formulation

We will use a simulation to concentrate on the modelling problem by making the setup simple. For this project, we will be working on the General Algebraic Modelling System (GAMS), which is specifically designed for modelling linear, nonlinear and mixed integer optimization problems. Our objective is to develop a

Mixed-Integer Linear Programming for which is applicable for both sharp and non-sharp separation. The system is especially useful with large, complex problems.

GAMS will help us to solve a formulation quickly and easily, as well as change the data to get different outcomes. From the split fraction calculated, we will formulate the simulation in GAMS.

3.4.1 **Logical Constraints**

Logical constraints were developed for the intermediate representation superstructure in **Figure 6** and **Figure 7** for the following purposes:

- to relate the continuous variables with the binary 0–1 variables, specifically to ensure that the non-selection of a process unit results in corresponding zero flowrates of the input and output streams associated with the process unit;
- to stipulate design specifications based on engineering knowledge and past design experience; and
- to enforce interconnectivity relationships among the states and tasks nodes in the superstructure.

The following notations and definitions are used in constructing these constraints:

$\boldsymbol{Y_i}$	Boolean variable with value true denoting the existence of a process unit *i* (including mixers and splitters) and values false denoting its non-existence
$\boldsymbol{y_i}$	binary variable associated with their corresponding Boolean variables with value equals to one (1) denoting the existence of a process unit *i* (including mixers and splitters) and value equals to zero (0) denoting its non-existence
$\mathbf{F}_j$	flow rate variable of a state (or material stream) *j*
$\boldsymbol{M_i}$	maximum capacity of a process unit i to represent the upper bound on its outlet flow rate in stream *j*

Note that in this work, it desirable to only consider the selection of the process units; thus, we have omitted the modelling of the stream selection in the logical constraints, which is commonly the case in problems of similar nature.

The logical constraints consist of design and structural specifications which have interconnectivity relationship. The logical constraints on structural specifications are categorized into two groups or sections:

(1) logical constraints on structural specifications that involve the overhead and bottom products;

(2) logical constraints on structural specifications that involve the feed or inlet to the columns.

The detailed specifications are also developed for the entire intermediate superstructure representation and they are included in Appendix A, Appendix B, Appendix C and Appendix D.

3.4.2 **Switching Constraints**

To ensure that the non-existence of a process unit results in the corresponding input flowrates to the unit assuming the value of zero, we consider the formulation of big-*M* logical constraints to impose the relations between the continuous variables, which in our case represent the flowrates of the streams, and the discrete binary 0–1 variables, which denote the existence of the streams and process units.

The big-*M* logical constraints (set to 10,000) are also sometimes termed as switching constraints. The main function of the switching constraints is to enforce the condition that no output flow exists if the unit does not exist.

The general formulation of the big-*M* logical constraints is given by:

$$F_t \leq M_t y_t \qquad \textbf{(9)}$$

where F_t = total flowrate of an input stream for process unit *t* in kg/day,

M_t = maximum capacity of process unit *t*

y_i = existence or non-existence of process unit *t*.

Constraint $F_t \leq M_t y_t$ (9) is related with the discrete binary variable where y_i can be ‘0’ or ‘1’.
When $y_i = 0$ (unit does not exist), then the constraint (9) becomes:

$$F_t \leq 0 \tag{10}$$

Flowrate variables however, are either zero or takes on positive values, so for constraint (10); $F_t = 0$, which stipulates the condition of zero input flowrate into a non-existing unit. When $y_t = 1$ (unit exists), then the constraint (9) becomes:

$$F_t \leq M_t \tag{11}$$

which means that the input flowrate is bounded from above by the value of the big-M constant. Here, it is clear that a suitable value for the big-M constant is the maximum capacity of the unit.

As mentioned, the main function of the switching constraints is to enforce the condition that no output flow exists if the unit does not exist. By extension, these constraints can be written as $F_i \leq M_i z_i$ to relate the stream flowrate to the binary variable z_i denoting the existence of the stream itself (instead of the unit from where it is produced). In our proposed approach, this is written for each column with the big-*M* constant, taken to be an arbitrarily large number, (bigger than 1000), which it acts as an upper bound for the corresponding feed flow rate of the initial mixture.

Refer to Appendix E: Switching constraints for the separation subsystem using intermediate representation.

3.4.3 **GAMS Software**

After defining the constraints for the streams and tasks, and the split fractions for components, an MILP formulation is developed using GAMS software to solve for the sequence of the separation.

The same approach is applied for all the cases (sharp and non-sharp separations) to synthesize the optimal sequence. The result is then compared with the typical industrial configuration.

3.5 Limitations and Assumptions

Due to limited source and time constraints, we have taken into account reliable and sensible assumptions to achieve the objective function.

The basic assumptions made are as follow:

1. Naphtha composition consists of hydrogen H_2, methane CH_4, ethane C_2H_6, ethene or ethylene C_2H_4, propane C_3H_8, propylene C_3H_6, butane C_4H_{10}, butene C_4H_8, 1,3-Butadiene C_4H_6 and cyclobutadiene C_4H_4.
2. Feed composition after pyrolysis that entering separation processes consists of hydrogen H_2, methane CH_4, ethane C_2H_6, ethene or ethylene C_2H_4, propane C_3H_8, propylene C_3H_6, propadiene C_3H_4, butane C_4H_{10}, butene C_4H_8, and 1, 3-Butadiene C_4H_6.
3. Each distillation column performs a simple split, i.e. one feed and two products consisting of the overhead products and bottom products.
4. For sharp separation case, each distillation column performs a sharp separation, i.e., each entering component leaves in only one product stream due to complete (100%) recovery.
5. The model-based optimization is based on a superstructure that embeds all possible alternatives for the design of an olefin production plant.

3.6 Gantt Chart and Key Milestones

No	Task	Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Start working on the GAMS code to solve for optimal sequence for ethylene production.		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩					
2	Compare the optimal sequence with typical industrial configuration for sharp separation.			🟩	🟩	🟩	🟩	🟩									
3	Address problem with non-sharp separation, giving infeasibility result.			🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩					
4	Check the constraints of the given problem, to identify the cause of the infeasibility						🟩	🟩	🟩	🟩	🟩						
5	Make necessary changes to the constraints and compare the result with the one closer to industrial configuration.						🟩	🟩	🟩	🟩	🟩	🟩	🟩				
6	Submission of Progress Report										🟥						
7	Check the switching constraints and objective function.								🟩	🟩	🟩	🟩					
8	Pre-EDX											🟥					
9	Examine the optimal flowsheet in Visio for sharp/non-sharp separation cases.										🟩	🟩	🟩				
10	Submission of Draft Report													🟥			
11	Submission of Dissertation & Technical Paper														🟥		
12	Oral Presentation															🟥	
13	Submission of Project Dissertation (Hard Bound)																🟥

- Key Milestones 🟥
- Process 🟩

CHAPTER 4:

COMPUTATIONAL EXPERIMENTS AND RESULTS

To demonstrate the implementation of the proposed model formulation for determining an optimal separation sequence, we consider different olefin feedstock (naphtha and ethane). Also, we have assessed different compositions of multi-components mixture (after cracking) for each of the feedstocks as shown in Table 2 and Table 3.

4.1 Split fractions

Based on the developed superstructures (refer to Figure 6 and Figure 7), the split fractions are tabulated for both sharp and non-sharp separation respectively as shown in Table 4 and Table 5. The data will be computed by the GAMS software to solve for Mixed-Integer Linear Programming optimization model on ethylene production plant.

Table 4: Split Fractions for Naphtha

Task		**Stream**		**Split Fraction**			
				Naphtha A	Naphtha B	Naphtha C	Naphtha D
Oil Fractionator		al		0.9754	0.9664	0.970482	0.961809
		m		0.0246	0.0336	0.029518	0.038191
C1	C1a	ab		0.128358	0.163411	0.15383	0.168234
		cl		0.871642	0.836589	0.84617	0.831766
	C1b	Sharp	ae	0.369489	0.446876	0.439221	0.521421
			fl	0.630511	0.553124	0.560779	0.478579
		Non-sharp	ah	0.4526002	0.538701	0.5272907	0.6114269
			fl	0.5473998	0.461299	0.4727093	0.3885731
	C1c	ak		0.690486	0.733715	0.734199	0.780564
		l		0.309514	0.266285	0.265801	0.219436
C2	C2a	ab		0.185895	0.222718	0.209521	0.215529
		ck		0.814105	0.777282	0.790479	0.784471
	C2b	ae		0.535115	0.609059	0.598231	0.668005
		fk		0.464885	0.390941	0.401769	0.331995
	C2c	Sharp	ah	0.787825	0.850035	0.831765	0.875502
			jk	0.212175	0.149965	0.168235	0.124498

		Non-sharp	ah	0.68482325	0.76099358	0.74342158	0.80321135
			fk	0.315176751	0.239006418	0.256578424	0.196788648
C3	C3a	ce		0.276641	0.338834	0.337273	0.424623
		fl		0.723359	0.661166	0.662727	0.575377
	C3b	ce		0.428962	0.497041	0.491739	0.576792
		fk		0.571038	0.502959	0.508261	0.423208
	C3c	ch		0.739376	0.807065	0.787174	0.841297
		jk		0.260624	0.192935	0.212826	0.158703
C4	C4a	cd		0.996173	0.990981	0.989884	0.97929
		e		0.003827	0.009019	0.010116	0.02071
	C4b	ad_fh		0.998304	0.995901	0.995273	0.989297
		e		0.001696	0.004099	0.004727	0.010703
	C4c	cd_fh		0.99778	0.994446	0.993681	0.985801
		e		0.00222	0.005554	0.006319	0.014199
C5	C5a	ab		0.23636	0.263089	0.253096	0.248841
		cd_fh		0.76364	0.736911	0.746904	0.751159
	C5b	ad		0.678686	0.715344	0.717897	0.760433
		fh		0.321314	0.284656	0.282103	0.239567
C6a		ab		0.348261	0.367779	0.352552	0.327236
		cd		0.651739	0.632221	0.647448	0.672764
C7a		cd		0.579234	0.613718	0.622303	0.68107
		fh		0.420766	0.386282	0.377697	0.31893
C8	C8a	fh		0.276748	0.319652	0.305755	0.338428
		jl		0.723252	0.680348	0.694245	0.661572
	C8b	fh		0.543596	0.616399	0.581265	0.625
		jk		0.456404	0.383601	0.418735	0.375
C9a		jk		0.321268	0.292391	0.317267	0.306931
		l		0.678732	0.707609	0.682733	0.693069

Table 5: Split fractions for Ethane

Task		**Stream**		**Split Fractions**		
				Ethane A	Ethane B	Ethane C
Oil Fractionator		al		0.9992	0.9952	0.9962
		m		0.0008	0.0048	0.0038
C1	C1a	ab		0.064351	0.104703	0.099478
		cl		0.935649	0.895297	0.900522
	C1b	Sharp	ae	0.951461	0.922126	0.926922
			fl	0.048539	0.077874	0.073078
		Non-sharp	ah	0.963028	0.935905	0.939712
			fl	0.036972	0.064095	0.060288
	C1c	ak		0.981785	0.96041	0.964164
		l		0.018215	0.03959	0.035836
C2	C2a	ab		0.065545	0.109019	0.103175
		ck		0.934455	0.890981	0.896825
	C2b	ae		0.969113	0.960138	0.961374
		fk		0.030887	0.039862	0.038626

	C2c	Sharp	ah	0.985219	0.980121	0.979802
			jk	0.014781	0.019879	0.020198
		Non-sharp	ah	0.98104	0.974875	0.974965
			fk	0.01896	0.025125	0.025035
C3	C3a		ce	0.948123	0.913019	0.91885
			fl	0.051877	0.086981	0.08115
	C3b		ce	0.966947	0.955261	0.956931
			fk	0.033053	0.044739	0.043069
	C3c		ch	0.984182	0.977689	0.977479
			jk	0.015818	0.022311	0.022521
C4	C4a		cd	0.998421	0.996066	0.99539
			e	0.001579	0.003934	0.00461
	C4b		ad_fh	0.998551	0.996584	0.995962
			e	0.001449	0.003416	0.004038
	C4c		cd_fh	0.998448	0.996157	0.995487
			e	0.001552	0.003843	0.004513
C5	C5a		ab	0.066625	0.111611	0.105729
			cd_fh	0.933375	0.888389	0.894271
	C5b		ad	0.983629	0.979542	0.981116
			fh	0.016371	0.020458	0.018884
C6a			ab	0.067734	0.113942	0.107764
			cd	0.932266	0.886058	0.892236
C7a			cd	0.98246	0.976971	0.978883
			fh	0.01754	0.023029	0.021117
C8	C8a		fh	0.325773	0.246452	0.243132
			jl	0.674227	0.753548	0.756868
	C8b		fh	0.521452	0.501312	0.477089
			jk	0.478548	0.498688	0.522911
C9a			jk	0.443425	0.325342	0.352087
			l	0.556575	0.674658	0.647913
			~~b~~	0.520995	0.404031	0.430878

Refer to Figure 6 and **Figure 7 for tasks and streams' units.

4.2 GAMS formulation

Referring to the obtained data from the split fractions together with the constraints developed, a coding is formulated using GAMS software.

Refer to Appendix F for GAMS formulation to synthesize the optimal sequence of ethylene separation for naphtha. Note that the formulation is same for ethane except for the split fractions.

4.3 Optimal Distillation Sequences

From the split fractions computed, we obtain the MILP model that gives the optimal sequence for olefin separations. Using the MILP model developed, we compare sequences using two types of feedstock to analyse the effects of different feedstock on the optimal sequences.

For each of the feedstock, we get the total flowrates and individual flowrates from each columns based on the selected task configurations.

The liquid naphtha with compositions shown in Table 2 is implemented in the proposed model and the optimal sequence for sharp separation obtained is shown in Table 6 below.

Table 6: Optimal Separation Sequences for Naphtha

	Selected Task (optimal)	**Flow (kg/hr)**	**Total Flow (kg/hr)**
Naphtha A	C1c	9754.000	26243
	C2c	6735.000	
	R1b	5306.000	
	R4	3019.000	
	C12	1429.000	
Naphtha B	C1c	9663.998	26418.62
	C2c	7090.622	
	R1b	6027.275	
	R4	2573.377	
	C12	1063.346	
Naphtha C	C1c	9704.823	26534.92
	C2c	7125.275	
	R1b	5926.556	
	R4	2579.548	
	C12	1198.719	
Naphtha D	C1c	9618.090	26743.72
	C2c	7507.538	
	R1b	6572.864	
	R4	2110.553	
	C12	934.673	

Optimal column sequence for the best possible solution for ethane feedstock is also obtained using the same model and tabulated in Table 7.

Table 7: Optimal Separation Sequences for Ethane

	Selected Task (optimal)	Flow (kg/hr)	Total Flow (kg/hr)
Ethane A	C1c	9992.000	29794.15
	C2c	9810.146	
	R1b	9664.955	
	R4	181.854	
	C12	145.190	
Ethane B	C1c	9952.000	29461.9
	C2c	9557.901	
	R1b	9367.699	
	R4	394.099	
	C12	190.202	
Ethane C	C1c	9962.000	29529.36
	C2c	9605.360	
	R1b	9411.332	
	R4	356.640	
	C12	194.028	

The superstructure representation for sharp separation of Naphtha A and Ethane A is illustrated in Figure 10 and Figure 11 respectively. The same representation is applicable for all different compositions of naphtha as well as ethane, with different flowrates.

For non-sharp separation, the same optimal sequence is selected owing to the GAMS result, suggesting that different approach of separation would give the same output, provided the constraints are same.

The optimal separation sequence obtained however does not follow the typical industry configuration for ethylene separation that follows the heuristic solutions. Our configuration suggests that the first column is debutanizer, followed by deethanizer, hydrogenation reactor, gasoline reactor and lastly extractive distillation. The column selected is lesser than the industrial configuration as shown in Figure 12 and Figure 13.

Earlier, we have modified the logical and switching constraints used in the mathematical formulation. The framework is somehow affecting our final output to produce optimal separation sequence. The employment of sharp and non-sharp separation however does not affect the separation.

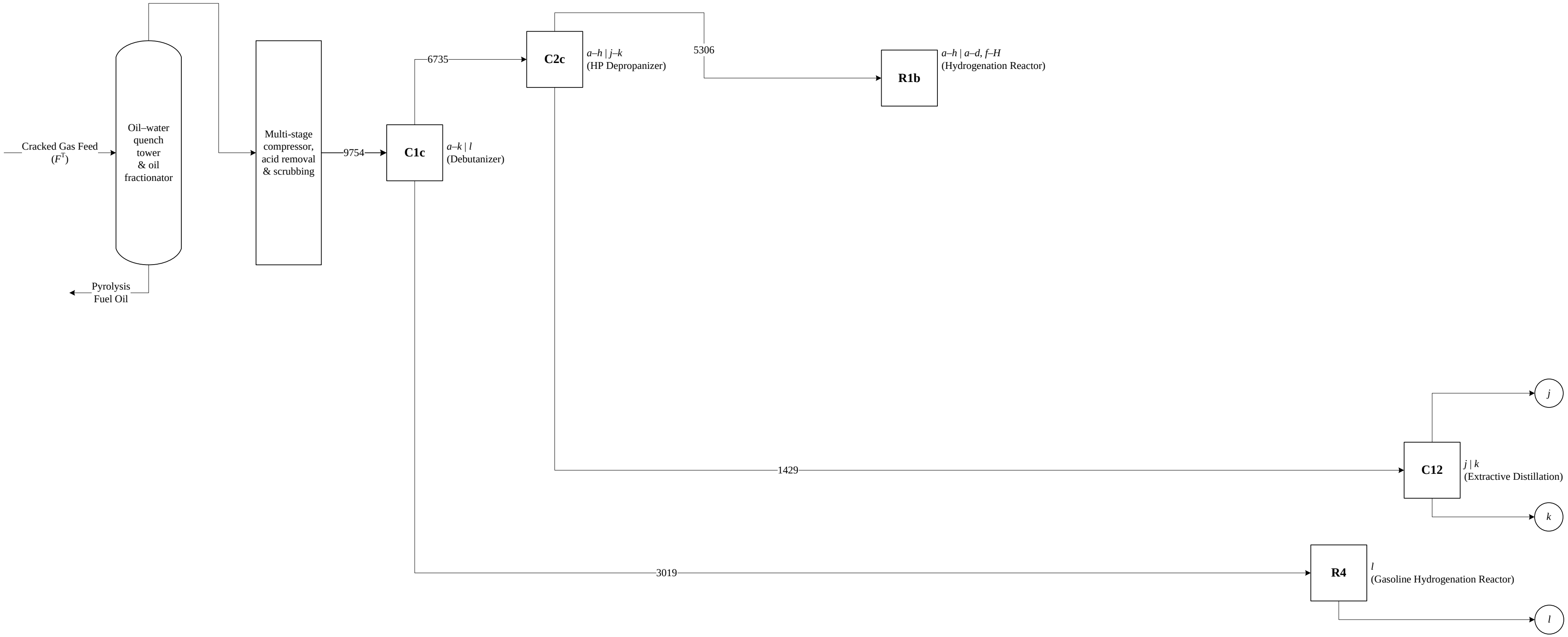


Figure 10: Superstructure representation for the sharp separation of Naphtha A composition.

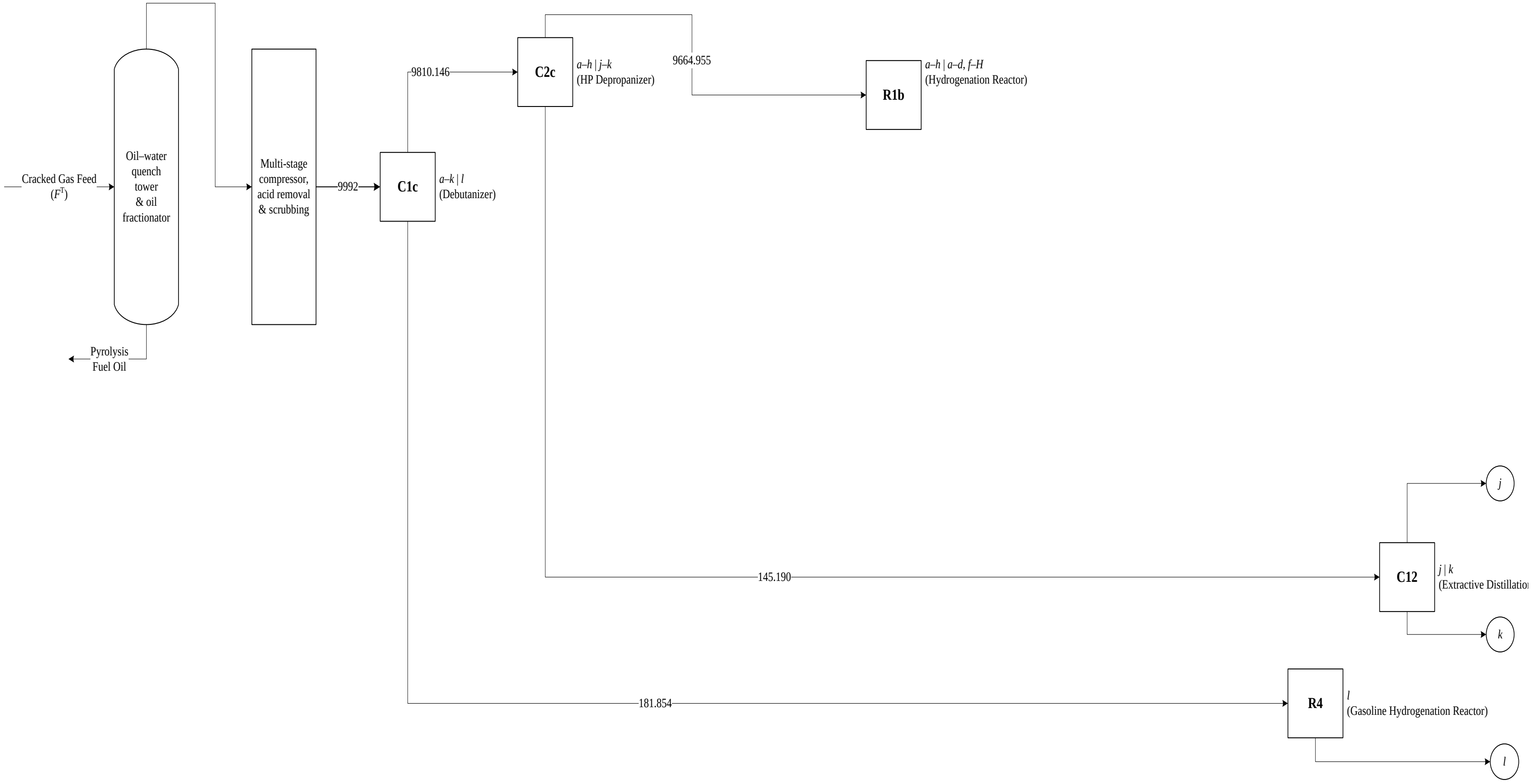


Figure 11: Superstructure representation for the sharp separation of Ethane A composition.

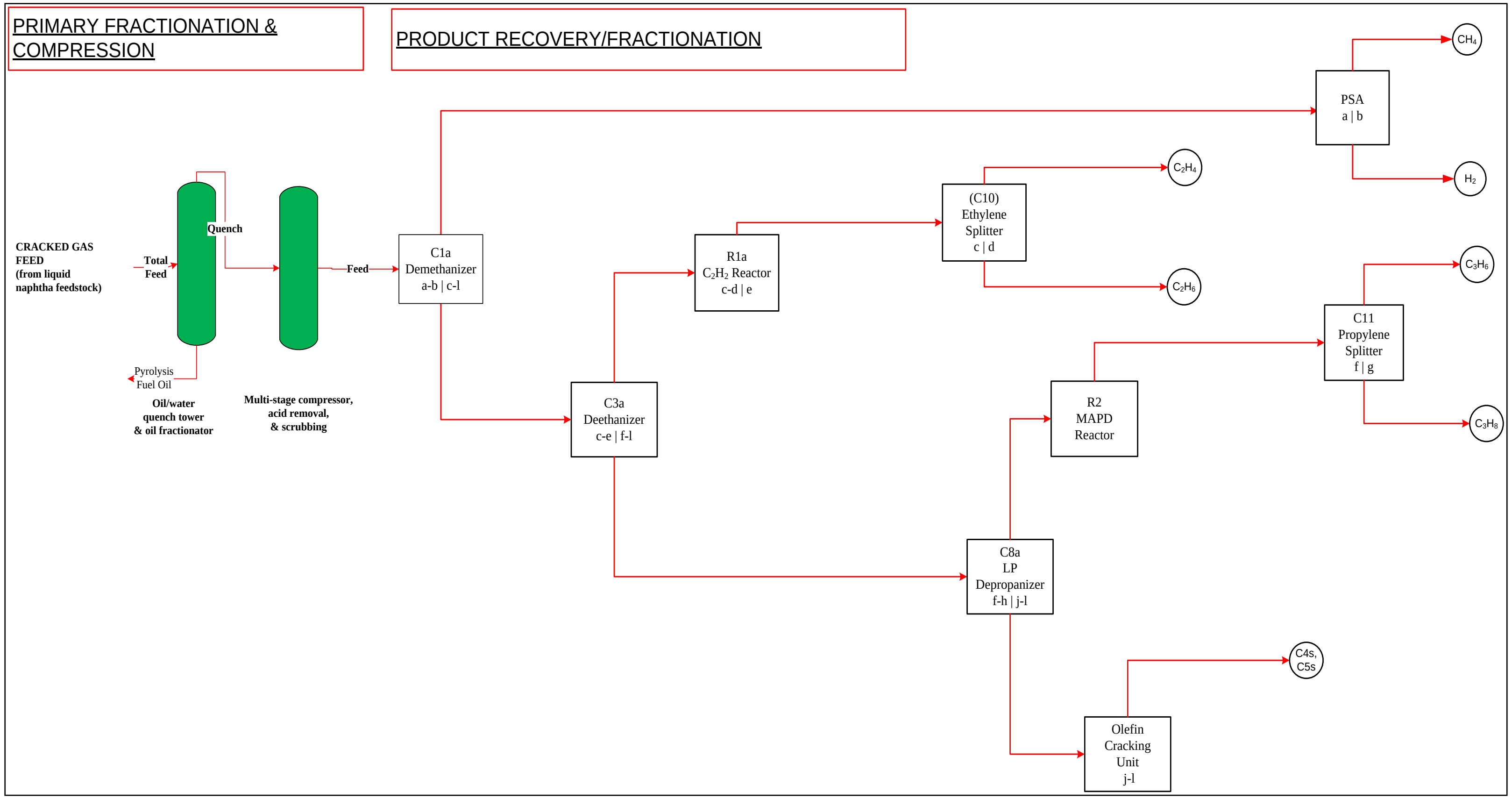


Figure 12: Optimal flowsheet for distillation sequencing using naphtha composition from University of Manchester's Centre for Process Integration (2005)

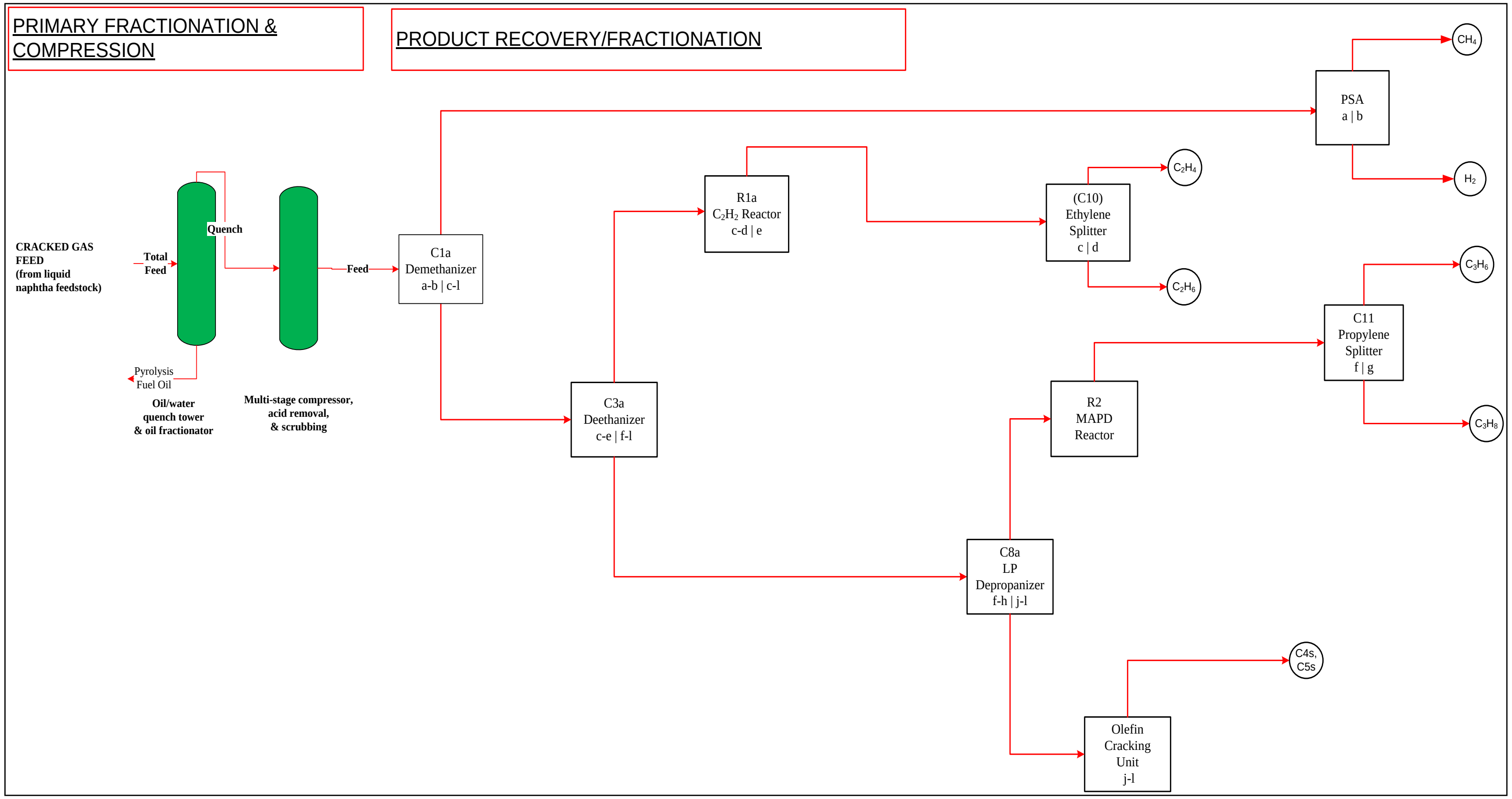


Figure 13: Optimal flowsheet distillation sequence for Ethane Feedstock from Ethylene Polyethylene (M) Sdn Bhd EPEMSB

CHAPTER 5:

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Each model required many hours of analyst and programming time to organize the data and write the programs that would transform the data into the form required by the mathematical programming. Particularly for this project, a mathematical expression, which is Mixed-Integer Linear Programming (MILP), is defined to simulate the processing of ethylene from various feedstocks.

Split fractions for each component are calculated, prior to constructing a superstructure that includes all possible separation sequences for olefins from naphtha and ethane.

The objective of the project is to find an optimal separation sequence, which follows most heuristic applied in the industry. The advantage of mathematical programming approaches is that they perform simultaneous optimisation of the sequence and operating conditions. However for this project, the constraints introduced in the formulation is affecting the separation sequence, giving a different pattern from typical industry configuration.

5.2 RECOMMENDATION

Several conclusions have been drawn according to the modelling and the optimization study, while the detailed discussions about their results will be discussed later.

To ensure a consistent and accurate model, care should be taken when applying assumptions to the process, for instance, yields compositions and feasibility of sharp separation for a column.

A more rigorous of objective function by considering the raw material cost, capital investment, production cost and profitability for the olefin production process in order to justify the feasibility of the olefin production. Feedstock availability should be emphasized to achieve efficient and cost-effective separations.

- Future work should consider a more reliable and flexible constraints for sharp and non-sharp separation to produce output closer to typical industrial configuration.

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APPENDICES

Appendix A: Constraints representation of logical relations as algebraic linear inequalities

Logical operator	Logic proposition	Logical Boolean expression	Representation as algebraic integer linear inequality/equality constraint
Logical OR		$Y_1 \vee Y_2 \vee \cdots \vee Y_r$	$y_1 + y_2 + \cdots + y_r \geq 1$
Logical AND		$Y_1 \wedge Y_2 \wedge \cdots \wedge Y_r$	$y_1 \geq 1$ $y_2 \geq 1$ $\cdots$ $y_r \geq 1$
Implication	$Y_1 \Rightarrow Y_2$ is logically equivalent to $\neg Y_1 \vee Y_2$	$\neg Y_1 \vee Y_2$	$(1 - y_1) + y_2 \geq 1$ $y_1 - y_2 \leq 0$ $y_1 \leq y_2$
Equivalence	Y_1 if and only if Y_2 $(Y_1 \Rightarrow Y_2) \wedge (Y_2 \Rightarrow Y_1)$ which can also be written as: $Y_1 \Leftrightarrow Y_2$	$(\neg Y_1 \vee Y_2) \wedge (\neg Y_2 \vee Y_1)$	$y_1 = y_2$
Exclusive OR (EOR)	Exactly one of the variables is true	$Y_1 \oplus Y_2 \oplus \cdots \oplus Y_r$	$y_1 + y_2 + \cdots + y_r = 1$
Classification	$Q = \{Y_1, Y_2, \ldots, Y_r\}$ Q is true if any of the variables inside the brackets are true		$y_q = y_1 + y_2 + \cdots + y_r$

Appendix B: Logical constraints on design specifications (DS) for the separation subsystem using intermediate representation

	Logic proposition on design specification	Logical expression and clauses	Integer linear inequality
DS1	Select only one from among: • demethanizer (task C1a) • HP depropanizer (task C1b) • debutanizer (C1c)	$Y_{a-b\|c-l}^{C1a} \oplus Y_{a-h\|f-l}^{C1b} \oplus Y_{a-k\|l}^{C1c}$	$y_{a-b\|c-l}^{C1a} + y_{a-h\|f-l}^{C1b} + y_{a-k\|l}^{C1c} = 1$
DS2	From among the demethanizer (C2a), deethanizer(C2b), and HP depropanizer (C2c), select none or only one (note: none of the task for C2 column can be selected because there is provision for it to be bypassed in the superstructure)	$Y_{a-b\|c-k}^{\mathrm{C2a}} \vee Y_{a-e\|f-k}^{\mathrm{C2b}} \vee Y_{a-h\|f-k}^{\mathrm{C2c}}$	$y_{a-b\|c-k}^{\mathrm{C2a}} + y_{a-e\|f-k}^{\mathrm{C2b}} + y_{a-h\|j-k}^{\mathrm{C2c}} \leq 1$
DS3	Select only one or none of the deethanizer (C3a, C3b) or debutanizer (C3c).	$Y_{c-e\|f-l}^{C3a} \vee Y_{c-e\|f-k}^{C3b} \vee Y_{c-h\|j-k}^{C3c}$	$y_{c-e\|f-l}^{C3a} + y_{c-e\|f-k}^{C3b} + y_{c-h\|j-k}^{C3c} \leq 1$
DS4	Catalytic hydrogenation reactor (R1) converts acetylene to ethane and ethylene. Components entering R1 depend on constraint DS1, i.e., whether HP depropanizer or debutanizer is selected upstream. (note that this might be a redundant constraint; this condition might have been enforced by other constraints)	$Y_{a-e\|a,c-d}^{R1A} \vee Y_{a-h\|a,c-d,f-h}^{R1b}$	$y_{a-e\|a,c-d}^{R1a} + y_{a-h\|a,c-d,f-h}^{R1b} \leq 1$
DS5	Extractive distillation column (C4) separates acetylene from the other components. As in previous, components entering C4 depend on the unit selected upstream.	$Y_{c-d\|e}^{C4a} \vee Y_{a-d,f-h\|e}^{C4b} \vee Y_{c-d,f-h\|e}^{C4c}$	$y_{c-d\|e}^{C4a} + y_{a-d,f-h\|e}^{C4b} + y_{c-d,f-h\|e}^{C4c} \leq 1$

DS6	Select at most one from among demethanizer (C5a), deethanizer (C5b), and depropanizer (C5c).		$y^{C5a}_{a-b\|c-d,f-h} + y^{C5b}_{a-d\|f-h} \leq 1$
DS7	Select only one or none from among LP depropanizer (C8a) and C8b	$Y^{C8a}_{f-h\|j-l} \vee Y^{C8b}_{f-h\|j-k}$	$y^{C8a}_{f-h\|j-l} + y^{C8b}_{f-h\|j-k} \leq 1$
DS8	At most two tasks can be selected between C4 hydrogenation reactor R3 and extractive distillation column C12		$y^{R3}_{j\|k} + y^{C12}_{j\|k} \leq 2$

Appendix C: Logical constraints on structural specifications for interconnectivity relationships for the separation subsystem using intermediate representation which involve the overhead and bottom products

Logic proposition on structural specification	Reformulation of logic proposition to algebraic constraint	Algebraic constraint (integer linear)
From the demethanizer (C1a): • **The overhead products go to the pressure swing absorber (PSA);** • **The bottom products go to the deethanizer (C3a).**	$Y_{a\vert b}^{\mathrm{C1a}} \Rightarrow Y_{a\vert b}^{\mathrm{PSA}} \wedge Y_{c-e\vert f-l}^{\mathrm{C3a}}$	$y_{a\vert b}^{\mathrm{PSA}} - y_{a\vert b}^{\mathrm{C1a}} \geq 0 \Rightarrow y_{a\vert b}^{\mathrm{PSA}} \geq y_{a\vert b}^{\mathrm{C1a}}$ $y_{c-e\vert f-l}^{\mathrm{C3a}} - y_{a,\vert b}^{\mathrm{C1a}} \geq 0$
From the HP depropanizer (C1b): • **The overhead products go to either the catalytic hydrogenation reactor (R1) or extractive distillation column (C4b)** • **The bottom products go to the LP depropanizer (C8a).**	$Y_{a-h\vert f-l}^{C1b} \Rightarrow \left(Y_{a-h\vert a,c-d,f-h}^{\mathrm{R1B}} \vee Y_{a-d,f-h\vert e}^{C4b}\right) \wedge Y_{f-h\vert j-l}^{C8a}$ $\neg Y_{a-h\vert f-l}^{C1b} \vee \left(\left(Y_{a-d,f-h\vert e}^{R1b} \vee Y_{a-d,f-h\vert e}^{C4b}\right) \wedge Y_{f-h\vert j-l}^{C8a}\right)$ $\left(\neg Y_{a-h\vert f-l}^{C1b} \vee \left(Y_{a-d,f-h\vert e}^{R1b} \vee Y_{a-d,f-h\vert e}^{C4b}\right)\right) \wedge \left(\neg Y_{a-h\vert f-l}^{C1b} \vee Y_{f-h\vert j-l}^{C8a}\right)$	$y_{a-d,f-h\vert e}^{R1b} + y_{a-d,f-h\vert e}^{C4b} - y_{a-h\vert f-l}^{C1b} \geq 0$ $y_{f-h\vert j-l}^{C8a} - y_{a-h\vert f-l}^{C1b} \geq 0$
From the debutanizer (C1c): • **The overhead products go to demethanizer (C2a), depropanizer (C2b) or debutanizer (C2c).** • **Bottom products go to gasoline hydrogenation reactor (R4).**	$Y_{a-k\vert l}^{C1c} \Rightarrow \left(Y_{a-b\vert c-k}^{C2a} \vee Y_{a-h\vert f-k}^{C2b} \vee Y_{a-i\vert j-k}^{C2c}\right) \wedge Y_{l}^{R4}$ $\neg Y_{a-k\vert l}^{C1c} \vee \left(\left(Y_{a-b\vert c-k}^{C2a} \vee Y_{a-h\vert f-k}^{C2b} \vee Y_{a-i\vert j-k}^{C2c}\right) \wedge Y_{l}^{R4}\right)$ $\left(\neg Y_{a-k\vert l}^{C1c} \vee Y_{a-b\vert c-k}^{C2a} \vee Y_{a-h\vert f-k}^{C2b} \vee Y_{a-i\vert j-k}^{C2c}\right) \wedge \left(\neg Y_{a-k\vert l}^{C1c} \vee Y_{l}^{R4}\right)$	$y_{a-b\vert c-k}^{C2a} + y_{a-h\vert f-k}^{C2b} + y_{a-i\vert j-k}^{C2c} - y_{a-k\vert l}^{C1c} \geq 0$ $y_{l}^{R4} - y_{a-k\vert l}^{C1c} \geq 0$

From the demethanizer (C2a): • **The overhead products go to pressure swing absorber (PSA)** • **The bottom products go to deethanizer(C3b) or debutanizer (C3c)**	$Y^{C2a}_{a-b\|c-k} \Rightarrow Y^{PSA}_{a\|b} \wedge \left(Y^{C3b}_{c-e\|f-k} \vee Y^{C3c}_{c-e\|j-k}\right)$ $\neg Y^{C2a}_{a-b\|c-k} \vee \left(Y^{PSA}_{a\|b} \wedge \left(Y^{C3b}_{c-e\|f-k} \vee Y^{C3c}_{c-e\|j-k}\right)\right)$ $\left(\neg Y^{C2a}_{a-b\|c-k} \vee Y^{PSA}_{a\|b}\right) \wedge \left(\neg Y^{C2a}_{a-b\|c-k} \vee Y^{C3b}_{c-e\|f-k} \vee Y^{C3c}_{c-e\|j-k}\right)$	$y^{PSA}_{a\|b} - y^{C2a}_{a-b\|c-k} \geq 0$ $y^{C3b}_{c-e\|f-k} + y^{C3c}_{c-e\|j-k} - y^{C2a}_{a-b\|c-k} \geq 0$
From the deethanizer (C2b): • **The overhead product go to catalytic hydrogenation reactor (R1)** • **The bottom product go to depropanizer (C8b)**	$Y^{C2b}_{a-e\|f-k} \Rightarrow Y^{R1}_{a-d,f-h\|e} \wedge Y^{C8b}_{f-h\|j-k}$ $\neg Y^{C2b}_{a-e\|f-k} \vee \left(Y^{R1}_{a-d,f-h\|e} \wedge Y^{C8b}_{f-h\|j-k}\right)$ $\left(\neg Y^{C2b}_{a-e\|f-k} \vee Y^{R1b}_{a-d,f-h\|e}\right) \wedge \left(\neg Y^{C2b}_{a-e\|f-k} \vee Y^{C8b}_{f-h\|j-k}\right)$	$y^{R1}_{a-d,f-h\|e} - y^{C2b}_{a-e\|f-k} \geq 0$ $y^{C8b}_{f-h\|j-k} - y^{C2b}_{a-h\|f-k} \geq 0$
From the deethanizer (C2c): • **The overhead product go to catalytic hydrogenation reactor (R1b)** • **The bottom product go to depropanizer (C8b)**	$Y^{C2c}_{a-h\|j-k} \Rightarrow \left(Y^{R1b}_{a-d,f-h\|e} \vee Y^{C4b}_{a-d,f-h\|e}\right) \wedge \left(Y^{C12}_{j\|k}\right)$ $\left(\neg Y^{C2c}_{a-h\|j-k} \vee Y^{R1b}_{a-d,f-h\|e} \vee Y^{C4b}_{a-d,f-h\|e}\right) \wedge \left(\neg Y^{C2c}_{a-h\|j-k} \vee Y^{C12}_{j\|k}\right)$	$y^{R1b}_{a-d,f-h\|e} + y^{C4b}_{a-d,f-h\|e} - y^{C2c}_{a-h\|j-k} \geq 0$ $y^{C12}_{j\|k} - y^{C2c}_{a-h\|j-k} \geq 0$
From the deethanizer (C3a): • **The overhead product go to catalytic hydrogenation reactor (R1a)** • **The bottom product go to depropanizer (C8b)**	$Y^{C3a}_{c-e\|f-l} \Rightarrow \left(Y^{R1a}_{c-d\|e} \vee Y^{C4a}_{c-d\|e}\right) \wedge Y^{C8a}_{f-h\|j-l}$ $\left(\neg Y^{C3a}_{c-e\|f-l} \vee Y^{R1a}_{c-d\|e} \vee Y^{C4a}_{c-d\|e}\right) \wedge \left(\neg Y^{C3a}_{c-e\|f-l} \vee Y^{C8a}_{f-h\|j-l}\right)$	$y^{R1a}_{c-d\|e} + y^{C4a}_{c-d\|e} - y^{C3a}_{c-e\|f-l} \geq 0$ $y^{C8a}_{f-h\|j-l} - y^{C3a}_{c-e\|f-l} \geq 0$
From the deethanizer (C3b): • **The overhead product go to catalytic hydrogenation reactor (R1a) or extractive distillation column (C4a)** • **The bottom product go to depropanizer**	$Y^{C3b}_{c-e\|f-k} \Rightarrow \left(Y^{R1a}_{c-d\|e} \vee Y^{C4a}_{c-d\|e}\right) \wedge Y^{C8b}_{f-h\|j-k}$ $\left(\neg Y^{C3b}_{c-e\|f-k} \vee Y^{R1a}_{c-d\|e} \vee Y^{C4a}_{c-d\|e}\right) \wedge \left(\neg Y^{C3b}_{c-e\|f-k} \vee Y^{C8b}_{f-h\|j-k}\right)$	$y^{R1a}_{c-d\|e} + y^{C4a}_{c-d\|e} - y^{C3b}_{c-e\|f-k} \geq 0$ $y^{C8b}_{f-h\|j-k} - y^{C3b}_{c-e\|f-k} \geq 0$

(C8b)		
From the deethanizer (C3c): • **The overhead product go to catalytic hydrogenation reactor (R1b) or extractive distillation column (C4a) or extractive distillation column (C4c)** • **Bottom products go to extractive distillation column (C12) or C4 hydrogenation reactor (R3).**	$Y^{C3c}_{c-h\vert j-k} \Rightarrow \left(Y^{R1c}_{c-d,f-h\vert e} \vee Y^{C4c}_{c-d,f-h\vert e}\right) \wedge \left(Y^{C12}_{j\vert k} \vee Y^{R3}_{j\vert k}\right)$ $\left(\neg Y^{C3c}_{3-9\vert 10,11} \vee Y^{R1c}_{c-d,f-h\vert e} \vee Y^{C4c}_{c-d,f-h\vert e}\right) \wedge \left(\neg Y^{C3c}_{3-9\vert 10,11} \vee Y^{C12}_{j\vert k} \vee Y^{R3}_{j\vert k}\right)$	$y^{R1c}_{c-d,f-h\vert e} + y^{C4c}_{c-d,f-h\vert e} - y^{C3c}_{c-h\vert j-k} \geq 0$ $y^{C12}_{j\vert k} + y^{R3}_{j\vert k} - y^{C3c}_{c-h\vert j-k} \geq 0$
Products from catalytic hydrogenation reactor (R1a) go to the demethaniser (C5a).	$Y^{R1a}_{c-d\vert e} \Rightarrow Y^{C5}_{a-d\vert f-h}$ $\neg Y^{R1a}_{c-d\vert e} \vee Y^{C5}_{a-d\vert f-h}$	$y^{C5}_{a-d\vert f-h} - y^{R1a}_{c-d\vert e} \geq 0$
Products from catalytic hydrogenation reactor (R1b) go to the demethaniser (C5b).	$Y^{R1b}_{c-d\vert e} \Rightarrow Y^{C5a}_{a-b\vert c-d,f-h}$ $\neg Y^{R1a}_{c-d\vert e} \vee Y^{C5a}_{a-b\vert c-d,f-h}$	$y^{C5a}_{a-b\vert c-d,f-h} - y^{R1b}_{c-d\vert e} \geq 0$
From extractive distillation (C4a): • **Overhead products of go to the methaniser (C5a)**	$Y^{C4a}_{c-d\vert e} \Rightarrow Y^{C5a}_{a-d\vert f-h}$ $\neg Y^{C4a}_{c-d\vert e} \vee Y^{C5a}_{a-d\vert f-h}$	$y^{C5b}_{a-d\vert f-h} - y^{C4a}_{c-d\vert e} \geq 0$
From extractive distillation (C4b) and (C4c): • **Overhead products go to deethanizer (C5a and C5b)**	$Y^{C4b}_{a-d,f-h\vert e} \Rightarrow Y^{C5a}_{a-b\vert c-d,f-h}$ $\neg Y^{C4b}_{a-d,f-h\vert e} \vee Y^{C5a}_{a-b\vert c-d,f-h}$ $Y^{C4c}_{c-d,f-h\vert e} \Rightarrow Y^{C5b}_{c-d\vert f-h}$ $\neg Y^{C4c}_{c-d,f-h\vert e} \vee Y^{C5b}_{c-d\vert f-h}$	$y^{C5a}_{a-b\vert c-d,f-h} - y^{C4b}_{a-d,f-h\vert e} \geq 0$ $y^{C5b}_{c-d\vert f-h} - y^{C4c}_{c-d,f-h\vert e} \geq 0$

From the demethaniser (C5a): • **Overhead products go to PSA** • **Bottom products go to deethanizer (C7)**	$Y^{C5a}_{a-b\|c-d,f-h} \Rightarrow Y^{PSA}_{a\|b} \wedge Y^{C7}_{c-d\|f-h}$ $\left(\neg Y^{C5a}_{a-b\|c-d,f-h} \vee Y^{PSA}_{a\|b}\right) \wedge \left(\neg Y^{C5a}_{a-b\|c-d,f-h} \vee Y^{C7}_{c-d\|f-h}\right)$	$y^{PSA}_{a\|b} - y^{C5a}_{a-b\|c-d,f-h} \geq 0$ $y^{C7}_{c-d\|f-h} - y^{C5a}_{a-b\|c-d,f-h} \geq 0$
From the demethanizer (C5b): • **Overhead products go to the demethaniser (C6)** • **Bottom products go to methyl acetylene & propadiene reactor (R2)**	$Y^{C5b}_{c-d\|f-h} \Rightarrow Y^{C6}_{a-b\|c-d} \wedge Y^{R2}_{f-h}$ $\left(\neg Y^{C5b}_{c-d\|f-h} \vee Y^{C6}_{a-b\|c-d}\right) \wedge \left(\neg Y^{C5b}_{c-d\|f-h} \vee Y^{R2}_{f-h}\right)$	$y^{C6}_{a-b\|c-d} - y^{C5b}_{c-d\|f-h} \geq 0$ $y^{R2}_{f-h} - y^{C5b}_{c-d\|f-h} \geq 0$
From the demethanizer (C6): • **Overhead products go to the PSA** • **Bottom product go to ethylene splitter (C10)**	$Y^{C6}_{a-b\|c-d} \Rightarrow Y^{PSA}_{a\|b} \wedge Y^{C10}_{c\|d}$ $\left(\neg Y^{C6}_{a-b\|c-d} \vee Y^{PSA}_{a\|b}\right) \wedge \left(\neg Y^{C6}_{a-b\|c-d} \vee Y^{C10}_{c\|d}\right)$	$y^{PSA}_{a\|b} - y^{C6}_{a-b\|c-d} \geq 0$ $y^{C10}_{c\|d} - y^{C6}_{a-b\|c-d} \geq 0$
From the deethanizer (C7): • **Overhead product go to ethylene splitter (C10)** • **Bottom product go to methyl acetylene & propadiene reactor (R2)**	$Y^{C7}_{c-d\|f-h} \Rightarrow Y^{C10}_{c\|d} \wedge Y^{R2}_{f-h}$ $\left(\neg Y^{C7}_{c-d\|f-h} \vee Y^{C10}_{c\|d}\right) \wedge \left(\neg Y^{C7}_{c-d\|f-h} \vee Y^{R2}_{f-h}\right)$	$y^{C10}_{c\|d} - y^{C7}_{c-d\|f-h} \geq 0$ $y^{R2}_{f-h} - y^{C7}_{c-d\|f-h} \geq 0$
From the depropanizer (C8a): • **Overhead products go to methyl acetylene & propadiene reactor (R2)** • **Bottom products will either got to debutanizer (C9) or olefin cracking unit (OCU)**	$Y^{C8a}_{f-h\|j-l} \Rightarrow Y^{R2}_{f-h} \wedge \left(Y^{C9}_{j-k\|l} \vee Y^{OCU}_{j-l}\right)$ $\left(\neg Y^{C8a}_{6-9\|10-12,14-18} \vee Y^{R2}_{f-h}\right) \wedge \left(\neg Y^{C8a}_{f-h\|j-l} \vee Y^{C9}_{j-k\|l} \vee Y^{OCU}_{j-l}\right)$	$y^{R2}_{f-h} - y^{C8a}_{f-h\|j-l} \geq 0$ $y^{C9}_{j-k\|l} + y^{OCU}_{j-l} - y^{C8a}_{f-h\|j-l} \geq 0$

From the depropanizer (C8b): • **Overhead products go to methyl acetylene and propadiene reactor (R2).** • **Bottom products will either go to C4 hydrogenation reactor (R3) or extractive distillation (C12)**	$Y_{f-h\|j-k}^{C8b} \Rightarrow Y_{f-h}^{R2} \wedge \left(Y_{j\|k}^{R3} \vee Y_{j\|k}^{C12}\right)$ $\left(\neg Y_{f-h\|j-k}^{C8b} \vee Y_{f-h}^{R2}\right) \wedge \left(\neg Y_{6-9\|10-11}^{C8b} \vee Y_{j\|k}^{R3} \vee Y_{j\|k}^{C12}\right)$	$y_{f-h}^{R2} - y_{f-h\|j-k}^{C8b} \geq 0$ $y_{j\|k}^{R3} + y_{j\|k}^{C12} - y_{f-h\|j-k}^{C8b} \geq 0$
From methyl acetylene and propadiene reactor (R2): • **Products go to propylene splitter (C11)**	$Y_{f-h}^{R2} \Leftrightarrow Y_{f\|g}^{C11}$ $\left(\neg Y_{f-h}^{R2} \vee Y_{f\|g}^{C11}\right) \wedge \left(Y_{f-h}^{R2} \vee \neg Y_{f\|g}^{C11}\right)$	$y_{f\|g}^{C11} - y_{f-h}^{R2} \geq 0$ $y_{f-h}^{R2} - y_{f\|g}^{C11} \geq 0$
From the debutanizer (C9): • **Overhead products will either go to C4 hydrogenation reactor (R3) or extractive distillation (C12)** • **Bottom products go to gasoline hydrogenation reactor (R4)**	$Y_{j-k\|l}^{C9} \Rightarrow \left(Y_{j\|k}^{R3} \vee Y_{j\|k}^{C12}\right) \wedge Y_{l}^{R4}$ $\left(\neg Y_{j-k\|l}^{C9} \vee Y_{j\|k}^{R3} \vee Y_{j\|k}^{C12}\right) \wedge \left(\neg Y_{j-k\|l}^{C9} \vee Y_{l}^{R4}\right)$	$y_{j\|k}^{R3} + y_{j\|k}^{C12} - y_{j-k\|l}^{C9} \geq 0$ $y_{l}^{R4} - y_{j-k\|l}^{C9} \geq 0$

Appendix D: Logic proposition on structural specification

Logic proposition on structural specification		Algebraic constraint (integer linear)
The inlet of demethanizer (C2a), depropanizer (C2b), and debutanizer (C2c) is the overhead product of debutanizer (C1c).	$Y^{C2a}_{a-b\|c-k} \vee Y^{C2b}_{a-h\|f-k} \vee Y^{C2c}_{a-h\|j-k} \Rightarrow Y^{C1c}_{a-k\|l}$ $\left(\neg Y^{C2a}_{a-b\|c-k} \vee Y^{C1c}_{a-k\|l}\right) \wedge \left(\neg Y^{C2b}_{a-h\|f-k} \vee Y^{C1c}_{a-k\|l}\right) \wedge \left(\neg Y^{C2c}_{a-h\|j-k} \vee Y^{C1c}_{a-k\|l}\right)$	$y^{C1c}_{a-k\|l} - y^{C2a}_{a-b\|c-k} \geq 0$ $y^{C1c}_{a-k\|l} - y^{C2b}_{a-h\|f-k} \geq 0$ $y^{C1c}_{a-k\|l} - y^{C2c}_{a-h\|j-k} \geq 0$
The inlet of deethanizer (C3a) is the bottom product of demethanizer (C1a).	$Y^{C3a}_{c-e\|f-l} \Rightarrow Y^{C1a}_{a-b\|c-l}$ $\neg Y^{C3a}_{c-e\|f-l} \vee Y^{C1a}_{a-b\|c-l}$	$y^{C1a}_{a-b\|c-l} - y^{C3a}_{c-e\|f-l} \geq 0$
The inlet of deethanizer (C3b) or debutanizer (C3c) is the bottom product of demethanizer (C2a).	$Y^{C3b}_{c-e\|f-k} \vee Y^{C3c}_{c-h\|j-k} \Rightarrow Y^{C2a}_{a-b\|c-k}$ $\neg\left(Y^{C3b}_{c-e\|f-k} \vee Y^{C3c}_{c-h\|j-k}\right) \vee Y^{C2a}_{a-b\|c-k}$ $\left(\neg Y^{C3b}_{c-e\|f-k} \wedge \neg Y^{C3c}_{c-h\|j-k}\right) \vee Y^{C2a}_{a-b\|c-k}$ $\left(\neg Y^{C3b}_{c-e\|f-k} \vee Y^{C2a}_{a-b\|c-k}\right) \wedge \left(\neg Y^{C3c}_{c-h\|j-k} \vee Y^{C2a}_{a-b\|c-k}\right)$	$y^{C2a}_{a-b\|c-k} - y^{C3b}_{c-e\|f-k} \geq 0$ $y^{C2a}_{a-b\|c-k} - y^{C3c}_{c-h\|j-k} \geq 0$
The inlet of catalytic hydrogenation reactor (R1a) is either from demethanizer (C3a) or demethanizer (C3b).	$Y^{R1a}_{c-d\|e} \Rightarrow Y^{C3a}_{c-e\|f-l} \vee Y^{C3b}_{c-e\|\|f-l}$ $\neg Y^{R1a}_{c-d\|e} \vee Y^{C3a}_{c-e\|f-l} \vee Y^{C3b}_{c-e\|\|f-l}$	$y^{C3a}_{c-e\|f-l} + y^{C3b}_{c-e\|\|f-l} - y^{R1a}_{c-d\|e} \geq 0$
The inlet of catalytic hydrogenation reactor (R1b) is either from depropanizer (C2b) , debutanizer (C2c) or HP depropanizer (C1b).	$Y^{R1b}_{a-d,f-h\|e} \Rightarrow Y^{C2b}_{a-h\|f-k} \vee Y^{C2c}_{a-h\|j-k} \vee Y^{C1b}_{a-h\|f-l}$ $\neg Y^{R1b}_{a-d,f-h\|e} \vee Y^{C2b}_{a-h\|f-k} \vee Y^{C2c}_{a-h\|j-k} \vee Y^{C1b}_{a-h\|f-l}$	$y^{C2b}_{a-h\|f-k} + y^{C2c}_{a-h\|j-k} + y^{C1b}_{a-h\|f-l} - y^{R1b}_{a-d,f-h\|e} \geq 0$
The inlet of catalytic hydrogenation reactor (R1c) is from debutanizer (C3c).	$Y^{R1c}_{c-d,f-h\|e} \Rightarrow Y^{C3c}_{c-h\|j-k}$ $\neg Y^{R1c}_{c-d,f-h\|e} \vee Y^{C3c}_{c-h\|j-k}$	$y^{C3c}_{c-h\|j-k} - y^{R1c}_{c-d,f-h\|e} \geq 0$

The inlet of extractive distillation (C4a) is either from deethanizer (C3a) or deethanizer (C3b).	$Y^{C4a}_{c-d\|e} \Rightarrow Y^{C3a}_{c-e\|f-l} \vee Y^{C3b}_{c-e\|f-k}$ $\neg Y^{C4a}_{c-d\|e} \vee Y^{C3a}_{c-e\|f-l} \vee Y^{C3b}_{c-e\|f-k}$	$y^{C3a}_{c-e\|f-l} + y^{C3b}_{c-e\|f-k} - y^{C4a}_{c-d\|e} \geq 0$
The inlet of extractive distillation (C4b) is either from depropanizer (C2b), debutanizer (C2c) or HP depropanizer (C1b).	$Y^{C4b}_{a-d,f-h\|e} \Rightarrow Y^{C2b}_{a-h\|f-k} \vee Y^{C2c}_{a-h\|j-k} \vee Y^{C1b}_{a-k\|l}$ $\neg Y^{C4b}_{a-d,f-h\|e} \vee Y^{C2b}_{a-h\|f-k} \vee Y^{C2c}_{a-h\|j-k} \vee Y^{C1b}_{a-k\|l}$	$y^{C2b}_{a-h\|f-k} + y^{C2c}_{a-h\|j-k} + y^{C1b}_{a-k\|l} - y^{C4b}_{a-d,f-h\|e} \geq 0$
The inlet of extractive distillation (C4c) is from debutanizer (C3c).	$Y^{C4c}_{c-d,f-h\|e} \Rightarrow Y^{C3c}_{c-h\|j-k}$ $\neg Y^{C4c}_{c-d,f-h\|e} \vee Y^{C3c}_{c-h\|j-k}$	$y^{C3c}_{c-h\|j-k} - y^{C4c}_{c-d,f-h\|e} \geq 0$
The inlet of demethanizer (C5a) or depropanizer (C5c) is either from catalytic hydrogenation reactor (R1b) or extractive distillation (C4b).	$Y^{C5a}_{a-b\|c-d,f-h} \vee Y^{C5c}_{a-d\|f-h} \Rightarrow Y^{R1b}_{a-d,f-h\|e} \vee Y^{C4b}_{a-d,f-h\|e}$ $(\neg Y^{C5a}_{a-b\|c-d,f-h} \wedge \neg Y^{C5c}_{a-d\|f-h}) \vee (Y^{R1b}_{1-4,6-9\|5} \vee Y^{C4b}_{1-4,6-9\|5})$	$y^{R1b}_{a-d,f-h\|e} + y^{C4b}_{a-d,f-h\|e} - y^{C5a}_{a-b\|c-d,f-h} \geq 0$ $y^{R1b}_{a-d,f-h\|e} + y^{C4b}_{a-d,f-h\|e} - y^{C5c}_{a-d\|f-h} \geq 0$
The inlet of deethanizer (C5b) is either from catalytic hydrogenation reactor (R1c) or extractive distillation (C4c).	$Y^{C5b}_{c-d\|f-h} \Rightarrow Y^{R1c}_{c-d,f-h\|e} \vee Y^{C4c}_{c-d,f-h\|e}$ $\neg Y^{C5b}_{c-d\|f-h} \vee Y^{R1c}_{c-d,f-h\|e} \vee Y^{C4c}_{c-d,f-h\|e}$	$y^{R1c}_{c-d,f-h\|e} + y^{C4c}_{c-d,f-h\|e} - y^{C5b}_{c-d\|f-h} \geq 0$
The inlet of demethanizer (C6) is from depropanizer (C5c).	$Y^{C6}_{a-b\|c-d} \Rightarrow Y^{C5c}_{a-d\|f-h}$ $\neg Y^{C6}_{a-b\|c-d} \vee Y^{C5c}_{a-d\|f-h}$	$y^{C5c}_{a-d\|f-h} - y^{C6}_{a-b\|c-d} \geq 0$
The inlet of deethanizer (C7) is from demethanizer (C5a).	$Y^{C7}_{c-d\|f-h} \Rightarrow Y^{C5a}_{a-b\|c-d,f-h}$ $\neg Y^{C7}_{c-d\|f-h} \vee Y^{C5a}_{a-b\|c-d,f-h}$	$y^{C5a}_{a-b\|c-d,f-h} - y^{C7}_{c-d\|f-h} \geq 0$
The inlet to depropanizer (C8a) is either from deethanizer (C3a) or HP depropanizer (C1b).	$Y^{C8a}_{f-h\|j-l} \Rightarrow Y^{C3a}_{c-e\|f-l} \vee Y^{C1b}_{a-h\|f-l}$ $\neg Y^{C8a}_{f-h\|j-l} \vee Y^{C3a}_{c-e\|f-l} \vee Y^{C1b}_{a-h\|f-l}$	$y^{C3a}_{c-e\|f-l} + y^{C1b}_{a-h\|f-l} - y^{C8a}_{f-h\|j-l} \geq 0$

The inlet to depropanizer (C8b) is either from deethanizer (C3b) or HP depropanizer (C2b).	$Y_{f-h\|j-k}^{C8b} \Rightarrow Y_{c-e\|f-k}^{C3b} \vee Y_{a-h\|f-k}^{C2b}$ $\neg Y_{f-h\|j-k}^{C8b} \vee Y_{c-e\|f-k}^{C3b} \vee Y_{a-h\|f-k}^{C2b}$	$y_{c-e\|f-k}^{C3b} + y_{a-h\|f-k}^{C2b} - y_{f-h\|j-k}^{C8b} \geq 0$
The inlet of olefin cracking unit (OCU) is either from depropanizer (C8a) or depropanizer (C8b).	$Y_{j-l}^{OCU} \Rightarrow Y_{f-h\|j-l}^{C8a} \vee Y_{f-h\|j-k}^{C8b}$ $\neg Y_{j-l}^{OCU} \vee Y_{f-h\|j-l}^{C8a} \vee Y_{f-h\|j-k}^{C8b}$	$y_{f-h\|j-l}^{C8a} + y_{f-h\|j-k}^{C8b} - y_{j-l}^{OCU} \geq 0$
The inlet of MAPD(R2) is from either from C7, C5b, C5c, C8a or C8b.	$Y_{f-h}^{R2} \Rightarrow Y_{c-d\|f-h}^{C7} \vee Y_{c-d\|f-h}^{C5b} \vee Y_{a-d\|f-h}^{C5c} \vee Y_{f-h\|j-l}^{C8a} \vee Y_{f-h\|j-k}^{C8b}$ $\neg Y_{f-h}^{R2} \vee Y_{c-d\|f-h}^{C7} \vee Y_{c-d\|f-h}^{C5b} \vee Y_{a-d\|f-h}^{C5c} \vee Y_{f-h\|j-l}^{C8a} \vee Y_{f-h\|j-k}^{C8b}$	$y_{c-d\|f-h}^{C7} + y_{c-d\|f-h}^{C5b} + y_{a-d\|f-h}^{C5c} + y_{f-h\|j-l}^{C8a} + y_{f-h\|j-k}^{C8b} - y_{f-h}^{R2} \geq 0$
The inlet to pressure swing absorber (PSA) is either from demethanizer (C1a), demethanizer (C2a), demethanizer (C5a) or demethanizer (C6).	$Y_{a\|b}^{PSA} \Rightarrow Y_{a-b\|c-l}^{C1a} \vee Y_{a-b\|c-k}^{C2a} \vee Y_{a-b\|c-d,f-h}^{C5a} \vee Y_{a-b\|c-d}^{C6}$ $\neg Y_{a\|b}^{PSA} \vee Y_{a-b\|c-l}^{C1a} \vee Y_{a-b\|c-k}^{C2a} \vee Y_{a-b\|c-d,f-h}^{C5a} \vee Y_{a-b\|c-d}^{C6}$	$y_{a-b\|c-l}^{C1a} + y_{a-b\|c-k}^{C2a} + y_{a-b\|c-d,f-h}^{C5a} + y_{a-b\|c-d}^{C6} - y_{a\|b}^{PSA} \geq 0$
The inlet of debutanizer (C9) is from depropanizer (C8a).	$Y_{j-k\|l}^{C9} \Rightarrow Y_{f-h\|j-l}^{C8a}$ $\neg Y_{j-k\|l}^{C9} \vee Y_{f-h\|j-l}^{C8a}$	$y_{f-h\|j-l}^{C8a} - y_{j-k\|l}^{C9} \geq 0$
The inlet to ethylene splitter (C10) is either from catalytic hydrogenation reator (R1a), extractive distillation (C4a), depropanizer (C5) or demethanizer (C6) or deethanizer (C7).	$Y_{c\|d}^{C10} \Rightarrow Y_{c-d\|e}^{R1a} \vee Y_{c-d\|e}^{C4a} \vee Y_{c-d\|f-h}^{C5b} \vee Y_{a-b\|c-d}^{C6} \vee Y_{c-d\|f-h}^{C7}$ $\neg Y_{c\|d}^{C10} \vee Y_{c-d\|e}^{R1a} \vee Y_{c-d\|e}^{C4a} \vee Y_{c-d\|f-h}^{C5b} \vee Y_{a-b\|c-d}^{C6} \vee Y_{c-d\|f-h}^{C7}$	$y_{c-d\|e}^{R1a} + y_{c-d\|e}^{C4a} + y_{c-d\|f-h}^{C5b} + y_{a-b\|c-d}^{C6} + y_{c-d\|f-h}^{C7} - y_{c\|d}^{C10} \geq 0$
The inlet of C11 is from MAPD (R2)	$Y_{f\|g}^{C11} \Rightarrow Y_{f-h}^{R2}$ $\neg Y_{f\|g}^{C11} \vee Y_{f-h}^{R2}$	$y_{f-h}^{R2} - y_{f\|g}^{C11} \geq 0$
The inlet to C4 hydrogenation reactor (R3) is either from debutanizer (C9), depropanizer (C8b), debutanizer (C3c) .	$Y_{j\|k}^{R3} \Rightarrow Y_{j-k\|l}^{C9} \vee Y_{f-h\|j-k}^{C8b} \vee Y_{c-h\|j-k}^{C3c}$ $\neg Y_{j\|k}^{R3} \vee \left(Y_{j-k\|l}^{C9} \vee Y_{f-h\|j-k}^{C8b} \vee Y_{c-h\|j-k}^{C3c} \right)$	$y_{j-k\|l}^{C9} + y_{f-h\|j-k}^{C8b} + y_{c-h\|j-k}^{C3c} - y_{j\|k}^{R3} \geq 0$

The inlet to extractive distillation (C12) is either from debutanizer (C9), depropanizer (C8b), debutanizer (C3c) or debutanizer (C2c).	$Y_{j\|k}^{C12} \Rightarrow Y_{j-k\|l}^{C9} \vee Y_{f-h\|j-k}^{C8b} \vee Y_{c-h\|j-k}^{C3c} \vee Y_{a-h\|j-k}^{C2c}$ $\neg Y_{j\|k}^{C12} \vee Y_{j-k\|l}^{C9} \vee Y_{f-h\|j-k}^{C8b} \vee Y_{c-h\|j-k}^{C3c} \vee Y_{a-h\|j-k}^{C2c}$	$y_{j-k\|l}^{C9} + y_{f-h\|j-k}^{C8b} + y_{c-h\|j-k}^{C3c} + y_{a-h\|j-k}^{C2c} - y_{j\|k}^{C12} \geq 0$
The inlet of gasoline dehydrogenation reactor (R4) is either from debutanizer (C9) or debutanizer (C1c).	$Y_{l}^{R4} \Rightarrow Y_{j-k\|l}^{C9} \vee Y_{a-k\|l}^{C1c}$ $\neg Y_{l}^{R4} \vee Y_{j-k\|l}^{C9} \vee Y_{a-k\|l}^{C1c}$	$y_{j-k\|l}^{C9} + y_{a-k\|l}^{C1c} - y_{l}^{R4} \geq 0$

Appendix E: Switching constraints for the separation subsystem using intermediate representation

Task/Process Unit	Switching Constraint
C1	$F^{\mathrm{C1}a} \leq M_{\mathrm{C1}a} y^{\mathrm{C1}a}$ $F^{\mathrm{C1}b} \leq M_{\mathrm{C1}b} y^{\mathrm{C1}b}$ $F^{\mathrm{C1}c} \leq M_{\mathrm{C1}c} y^{\mathrm{C1}c}$
C2	$F^{\mathrm{C2}a} \leq M_{\mathrm{C2}a} y^{\mathrm{C2}a}$ $F^{\mathrm{C2}b} \leq M_{\mathrm{C2}b} y^{\mathrm{C2}b}$ $F^{\mathrm{C2}c} \leq M_{\mathrm{C2}c} y^{\mathrm{C2}c}$
C3	$F^{\mathrm{C3}a} \leq M_{\mathrm{C3}a} y^{\mathrm{C3}a}$ $F^{\mathrm{C3}b} \leq M_{\mathrm{C3}b} y^{\mathrm{C3}b}$ $F^{\mathrm{C3}c} \leq M_{\mathrm{C3}c} y^{\mathrm{C3}c}$
R1	$F^{\mathrm{R1a}} \leq M_{\mathrm{R1}a} y^{\mathrm{R1}a}$ $F^{\mathrm{R1b}} \leq M_{\mathrm{R1}b} y^{\mathrm{R1}b}$ $F^{\mathrm{R1c}} \leq M_{\mathrm{R1}b} y^{\mathrm{R1c}}$
C4	$F^{\mathrm{C4}a} \leq M_{\mathrm{C4}a} y^{\mathrm{C4}a}$ $F^{\mathrm{C4}b} \leq M_{\mathrm{C4}b} y^{\mathrm{C4}b}$ $F^{\mathrm{C4}c} \leq M_{\mathrm{C4}c} y^{\mathrm{C4}c}$
C5	$F^{\mathrm{C5}a} \leq M_{\mathrm{C5}a} y^{\mathrm{C5}a}$ $F^{\mathrm{C5}b} \leq M_{\mathrm{C5}b} y^{\mathrm{C5}b}$ $F^{\mathrm{C5}c} \leq M_{\mathrm{C5}c} y^{\mathrm{C5}c}$
C6	$F^{\mathrm{C6}} \leq M_{\mathrm{C6}} y^{\mathrm{C6}}$
C7	$F^{\mathrm{C7}} \leq M_{\mathrm{C7}} y^{\mathrm{C7}}$
C8	$F^{\mathrm{C8}a} \leq M_{\mathrm{C8}a} y^{\mathrm{C8}a}$ $F^{\mathrm{C8}b} \leq M_{\mathrm{C8}b} y^{\mathrm{C8}b}$
R2	$F^{\mathrm{R2}} \leq M_{\mathrm{R2}} y^{\mathrm{R2}}$
C9	$F^{\mathrm{C9}} \leq M_{\mathrm{C9}} y^{\mathrm{C9}}$
C10	$F^{\mathrm{C10}} \leq M_{\mathrm{C10}} y^{\mathrm{C10}}$
C11	$F^{R2}_{8,9\rightarrow 6,7} \leq M_{\mathrm{C11}} y^{\mathrm{C11}}_{6\mid 7}$
R3	$F^{\mathrm{R3}} \leq M_{\mathrm{R3}} y^{\mathrm{R3}}$

C12	$F^{\mathrm{C12}} \le M_{\mathrm{C12}} y^{\mathrm{C12}}$
Pressure Swing Absorber (PSA)	$F^{\mathrm{PSA}} \le M_{\mathrm{PSA}} y^{\mathrm{PSA}}$
Olefin Cracking Unit (OCU)	$F_{\mathrm{OCU}} \le M_{\mathrm{OCU}} y^{\mathrm{OCU}}$
R4	$F^{R4} \le M_{\mathrm{R4}} y^{R4}$

Appendix F: GAMS Formulation for Naphtha A

```
$Title: Naphtha A Separation
$EOLCOM #
*==============================================================================
*Declaration of Sets
*==============================================================================
SETS
*the set of all tasks in superstructure
T     Task in a distillation column or reactor
/
Oil_Fractionator
Quench_Fractionator
FEED
C1a,C1b,C1c,C2a,C2b,C2c,C3a,C3b,C3c,PSA,R1a,R1b,C4a,C4b,C4c,C5a,C5b,C8a,C8b,R2,R3,R4,C12,C11,C10,C9,C7,C6
OCU,
/
U     Equipment (distillation column or reactor) associated with  tasks
/
C1,C2,C3,C4,R1,R2,R3,R4,C8,C12,PSA,C10
/
S        Set of intermediate products (or streams or components)
/
al,m,ab,cl,ah,fl,ak,l,ck,fk,jk,ce,ch,cd,ad_fh,cd_fh,ad,fh,jl,ae,a,b,fg,b_fh,b_k,bk
/
$onecho >taskin.txt
dset=S rng=Naphtha_D.SHARP.GAMS!B2:G4 rdim=2
$offecho
pm(T,S)      set maps a task to its intermediate product streams (streams produced by a task)
/
C1A.(ab,cl)
* change C1B.(ah,fl)  to C1B.(ae,fl) for sharp - Nik
C1B.(ae,fl),C1C.(ak,l),C2A.(ab,ck),C2B.(ae,fk)
* change C2C.(ah,fk) to C2C.(ah,jk) for sharp - Nik
C2C.(ah,jk),C3A.(ce,fl),C3B.(ce,fk),C3C.(ch,jk),R1A.ad,R1B.ad_fh,C4A.cd,C4B.ad_fh,C4C.cd_fh,C5A.(ab,cd_fh),
C5B.(ad,fh),C6.(ab,cd),C7.(cd,fh),C8A.(fh,jl),C8B.(fh,jk),R2.fg,C9.(jk,l),
```

```
/
fm(T,S)     set maps a task to the intermediate product streams that feed the task (materials streams directed to a column)
/
(C2A,C2B,C2C).ak,C3A.cl,(C3B,C3C).ck,R1A.ae,R1B.ah,C4A.ce,C4B.ad_fh,
C4C.cd_fh,(C5A,C5B).ad_fh,C6.ad,C7.cd_fh,C8A.fl,C8B.fk,
*R2.b_fh
R2.fh,C9.jl,OCU.jl,R4.l,PSA.ab,C10.cd,C11.fg,C12.jk,R3.b_k,
/
task_producing_IP(T,S)    set for logical constraints on structural specifications for tasks producing intermediate products (IP)
/
C1A.(ab,cl)
* change C1B.(ah,fl)  to C1B.(ae,fl) for sharp - Nik
C1B.(ae,fl),C1C.(ak,l),C2A.(ab,ck),C2B.(ae,fk),
* change C2C.(ah,fk) to C2C.(ah,jk) for sharp - Nik
C2C.(ah,jk),C3A.(ce,fl),C3B.(ce,fk),C3C.(ch,jk),C4A.cd,
*C4B.ad_fh
C4B.ah
*C4C.cd_fh
C4C.ch
*Component "e" is not considered because it is a terminal product of C4 (and not an intermediate product)
R1A.ad,R1B.ad_fh,C5A.(ab,cd_fh),C5B.(ad,fh),C6.(ab,cd),C7.(cd,fh),C8A.(fh,jl),C8B.(fh,jk),C9.(jk,l),R2.fg
/
IP_feed_to_task(T,S)     set for logical constraints on structural specifications connecting a feed stream to a task
/
PSA.ab,C2A.ak,C2B.ak,C2C.ak,C3A.cl,C3B.ck,C3C.ck,R1a.ae,R1b.ah,
C4a.ce,C4b.ah,C4C.ch,C5a.ad_fh,C5B.ad_fh,C6.ad,C7.cd_fh,C8A.fl,
C8B.fk,C9.jl,R2.fh,R3.b_k,C10.cd,C11.fg,C12.jk,R4.l,OCU.jl
/
outlet_column(T,S)
/
(C2a,C2b,C2c).ak,C3a.cl,(C3b,C3c).ck,R1a.ae,(R1b,C4b).ah,C4a.ce,(C4c,C7).ch,PSA.ab,
C8a.fl,R4.l,C8b.fk,C12.jk,R1b.cd_fh,(R3).jk,C10.cd,,(C5a,C5b).ad_fh,R2.fh,C6.ad,(OCU,C9).jl
/
column(T,S)
/
C1a.(ab,cl)
```

```
*C1a.ab
*C1a.cl
* change C1b.(ah,fl)  to C1b.(ae,fl) for sharp - Nik
C1b.(ae,fl),C1c.(ak,l),C2a.(ab,ck),C2b.(ae,fk)
* no change for C2c.(ah,jk)for sharp - Nik
C2c.(ah,jk),C3a.(ce,fl),C3b.(ce,fk),C3c.(ch,jk),C4a.cd,C4b.ad_fh,C4c.cd_fh,R1a.cd,R1b.cd_fh,
C5a.(ab,cd_fh),C5b.(ad,fh),C6.(ab,cd),C7.(cd,fh),C8a.(fh,jl),C8b.(fh,jk),C9.(jk,l)
/
;
ALIAS (S,S1);
AlIAS (T,T1);
*================================================================================
*Declaration of Parameters for rest of model
*================================================================================
PARAMETER
M(T)   Big M Constant-1000 is the upper bound as it corresponds to the feed flow rate of the intial mixture;
M(T) = 1E4;
*Original value: M(T) = 100000;
PARAMETER
spltfrc(T,S)       Split fraction maps unit to intermediate product streams (exclude tasks producing terminal products including component "e")
/
QUENCH_FRACTIONATOR.al   0.9754,
OIL_FRACTIONATOR.m       0.0246,
C1a.ab         0.128357597,
C1a.cl         0.871642403,
C1b.ae         0.36948944,
C1b.fl         0.63051056,
C1c.ak         0.690485954,
C1c.l          0.309514046,
C2a.ab         0.185894581,
C2a.ck         0.814105419,
C2b.ae         0.535115071,
C2b.fk         0.464884929,
C2c.ah         0.787824796,
C2c.jk         0.212175204,
C3a.ce         0.27664079,
```

```
C3a.fl      0.72335921,
C3b.ce      0.428962247,
C3b.fk      0.571037753,
C3c.ch      0.739376254,
C3c.jk      0.260623746,
C4a.cd      0.996173469,
C4b.ad_fh     0.998303807,
C4c.cd_fh     0.99777997,
C5a.ab      0.236360204,
C5a.cd_fh     0.763639796,
C5b.ad      0.678686049,
C5b.fh      0.321313951,
C6.ab       0.348261474,
C6.cd       0.651738526,
C7.cd       0.579233622,
C7.fh       0.420766378,
C8a.fh      0.276747967,
C8a.jl      0.723252033,
C8b.fh      0.543596295,
C8b.jk      0.456403705,
C9.jk       0.321267986,
C9.l        0.678732014
*C10.c
*C10.d
*R1b.cd_fh     1.0
/
Fixed_Cost(T)     Fixed Cost per year
/
OIL_Fractionator      90000,
QUENCH_Fractionator     95000,
FEED                   1,
C1a               105000,
C1b               105000,
C1c               105000,
PSA                85000,
C2a               115000,
```

```
C2b               115000,
C2c               115000,
C3a               140000,
C3b               140000,
C3c               140000,
C4a               120000,
C4b               120000,
C4c               120000,
R1a                200000,
R1b                200000,
R2                20000,
C5a               120000,
C5b               120000,
C6               125000,
C7               125000,
C8a               145000,
C8b               145000,
C9               145000,
C10               155000,
C11               155000,
C12               145000,
R3                25000,
R4                25000,
OCU                800000
/
Operating_Cost(T)    Operating Cost per column or task per year
;
Operating_Cost(T) = 12000;
;
*==============================================================================
*Define scalar quantities for rest of model
*==============================================================================
SCALARS
Plant_Life     total life span of plant in operation     /20/
TOTFEED  total feed flow rate to superstructure   /10000/
epsilon /0.001/
```

```
;
*=========================================================================================
*Declaration of variables
*=========================================================================================
FREE VARIABLE
Z       Objective function
;
BINARY VARIABLES
Y(T)      Columns selection in superstruture associated with T Tasks(existance Or Non-existance)
;
POSITIVE VARIABLES
F(T)      Flow Rate of selected T task associated with S streams
Fraction(T)
;
*=========================================================================================
*Declaration of Equations
*=========================================================================================
*for material balances around units
*for logical constraitns on design specifications, structural specifications.
*for switching constraints
EQUATIONS
OBJECTIVE       Objective function
distillate_of_total_feed
bottoms_of_total_feed
MB_Unit         Material Balances for Unit
*MB_C5
*Design Specifications
DS1,DS2,DS3,DS4,DS5,DS6a,DS6bDS7,DS9,DS8
*Structural specifications
Inlet(T,S)        Inlet Condition
STRUCTURAL_SPEC_LC(T,S)  Overhead & Bottom
BigM(T)            Big M Logical Constraints-Switching Constraints with T tasks
INTEGER_CUT_1
;
********Objective Function*****************************************************
*OBJECTIVE..     Z=E= SUM(T, Fixed_Cost(T)*F(T));
```

```
OBJECTIVE..      Z =E= SUM ( T, ( Fixed_Cost(T)/Plant_Life) * Y(T) ) + SUM ( T, Operating_Cost(T) * F(T) );

*OBJECTIVE..      Z =E= 1;

*Initial Feed to Superstructure

distillate_of_total_feed..  F('QUENCH_FRACTIONATOR') =E= spltfrc('QUENCH_FRACTIONATOR','al') * TOTFEED

;

bottoms_of_total_feed..  F('OIL_FRACTIONATOR') =E= spltfrc('OIL_FRACTIONATOR','m') * TOTFEED

;

*Unit/Task

MB_Unit(S)..    SUM ( T $ pm(T,S), spltfrc(T,S)*F(T)) =E= SUM(T $ fm(T,S),F(T));

*sharp

MB_Unit_8('fk')..  0.464884929*F('C2b') + 0.571037753*F('C3b') - F('C8b') =E= 0

;

MB_Unit_9('jk')..  0.212175204*F('C2c') + 0.260623746*F('C3c') + 0.456403705*F('C8b') + 0.321267986*F('C9') =E=
F('C12')

;

MB_C11..         F('R2')=E=F('C11');

*MB_C5..         F('R1b')=E=F('C7');

*Only One Task is selected for Every unit

DS1..     Y('C1a')+ Y('C1b')+Y('C1c') =E= 1;

*No more than 1 process allowed( none or 1 process selected)

DS2..     Y('C2a')+ Y('C2b')+Y('C2c')=L=1;

DS3..     Y('C3a')+ Y('C3b')+Y('C3c')=L=1;

DS4..     Y('R1a')+ Y('R1b')=L=1;

DS5..     Y('C4a')+ Y('C4b')+Y('C4c')=L=1;

*More than 1 process allowed( None, 1 or 2 process selected)

DS6a..    Y('R1a')+ Y('C4a')=L=2;

DS6b..    Y('R1b')+Y('C4b')=L=2;

*No more than 1 process allowed( none or 1 process selected)

DS7..     Y('C5a')+ Y('C5b')=L=1;

DS8..     Y('C8a')+ Y('C8b')=L=1;

*More than 1 process allowed( None, 1 or 2 process selected)

DS9..     Y('R3')+ Y('C12')=L=2;

*Big-M Logical Constraints

BigM(T)..      F(T) =L= M(T) * Y(T)

;

BigM_1('FEED')..  F('FEED') =L= 10100*Y('FEED');

*
```

```
*Limit Choice of Overhead & Bottom
INTEGER_CUT_1..
Y('C1c') + Y('C2c') + Y('R1b') + Y('R4') + Y('C12') =L= 4;
InletC5a..  Y('C4a') + Y('C4b') + Y('R1b') - Y('C5a')=G=0;
MODEL NAPHTHA
/
*ALL
OBJECTIVE

distillate_of_total_feed
bottoms_of_total_feed

*MB_Unit
MB_Unit_1
DS1,DS2,DS7

/;
*Intial values and bound are given to avoid getting stuck at an infeasible point wen the NLP solver starts up
F.up(T)=TOTFEED;
Y.up(T)=1;
*OPTION
OPTION
MIP = CPLEX
LIMROW = 100000
LIMCOL = 100000
OPTCA = 0
OPTCR = 0
;
SOLVE NAPHTHA USING MIP MINIMIZING Z
;
DISPLAY Z.L, Y.L, F.L;
```