Optimization Approaches & Strategies for Distillation Column Sequencing Separation for Olefins Production

by

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ID: 7045

Dissertation submitted in partial fulfillment of the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

____
(KHOR CHENG SEONG)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2009

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.

____
(LEE TZU FEN)

ACKNOWLEDGEMENTS

Firstly, I would like to acknowledge the guidance given by my supervisor, Mr. Khor Cheng Seong throughout the whole period of completing this final year project. His patience and kindness help has been the main the main source of motivation and driven me in completing the project successfully.

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Finally, I would like to thank all my fellow colleagues for their assistance and ideas in completion of this project.

ABSTRACT

This main objective of this project is to develop a mathematical model for determining the optimal design of distillation sequencing for olefin production. The mathematical model with optimization procedure for the integration of olefin flow from refinery to a petrochemical plant is based on a process flowsheet superstructure representation that embeds all possible alternatives for the distillation sequencing. The model formulation includes material balances with fixed split fractions and logical constraints for representing design specifications and structural specifications based on engineering knowledge and past design experience and heuristics. Additionally, big-M logical constraints relating the continuous variables of flowrates to the binary 0–1 variables of column existence are incorporated. In this work, the intermediate superstructure representation is adopted to represent the distillation sequencing for olefin production because it has been shown to provide good computational performance in obtaining the global optimal solution (Caballero and Grossmann, 1999). The optimization model is investigated using different feedstock; ethane from Ethylene Polyethylene (M) Sdn. Bhd (EPEMSB) and naphtha from University of Manchester's Process Integration (2005). By using different feedstocks, the computational results yield the same optimal sequencing. Furthermore, ~~The~~ the optimal distillation sequencing with this model formulation is validated with the existing olefin plant. It is proved that the optimal distillation sequencing is consistent with the common heuristic in process plant synthesis. The optimization model is also investigated using integer cuts in order to check that they agree or conform to the heuristic for distillation sequencing. It is proved that the optimum solution has the least total mass flow rate.

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ABBREVIATIONS & NOMENCLATURE

The following abbreviations and nomenclatures are used throughout this interim report.

Abbrev.	Full name
STN	State Task Network
SEN	State Equipment N~~n~~etwork

~~s~~Sets and I~~i~~ndices

i	process units
j	process streams
k	~~final product~~task as represented by a column

Parameters

TOTFEED	total feed flowrate
SPLTFRC(T,S)	split fraction associated with task and stream

Continuous Variables

F(T)	Flowrate associated with task
FSm	set of all columns having intermediate product m as feed
PSm	set of all columns that produce a given intermediate product m as distillate or bottoms
IP	set of all intermediate products

~~b~~Binary V~~v~~ariables

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y_i	existence of process unit *i*
z_j	existence of material stream *j*

~~where PSm is the set of all columns that produce a given intermediate product m as distillate or bottoms,~~
~~FSm is the set of all columns having intermediate product m as feed,~~
~~IP is the set of all intermediate products~~

CHAPTER 1

INTRODUCTION

1.1. Background Of Study

The goal of conceptual design (process synthesis) is 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 three major approaches for determining an optimal topology or configuration of a petrochemical plant:

1) The heuristic and evolutionary approach
   Heuristic method proposed by douglas relies on intuition and engineering knowledge. This method uses the ‘onion diagram’ approach where it considers the critical equipment like the reactors before progressing to the separation units and finally to heat transfer units. Douglas’s method enables flow sheet structures to be determined at near optimal solution and at a faster time. (douglas, 1988)

2) Thermodynamic targets and physical insight approach (linnhoff et all., 1993)
   This method exploits the basic physical principles such as thermodynamics like pinch technology. This approach yields designs that features high energy efficiency and often near optimal solutions.

3) Algorithmic approach (Grossmann, 1996)
   The algorithmic approach uses mathematical programming techniques. The formulation is based upon a superstructure that represents all possible process

flow sheets. It includes the simultaneous and rigorous considerations of all factors.

The study is aimed at exploring the third approach which is the algorithm approach to obtain the methodology for an optimal naphtha separation topology design.

1.2. Problem Statement

The problem addressed in this study can be stated as follows: given are the availability and composition olefin feedstock, product demands, coefficient for fixed cost and variable cost, and availability of process units in terms of different choices of task and equipment, and the interconnections among them. The problem in this study is to synthesize the optimal flow sheet distillation sequence and satisfies the criteria of cost.

The basic assumptions made in this study are:

1. Each distillation column performs a simple split. (i.e. One feed and two products)
2. Each distillation column performs a sharp separation (i.e. a component appears entirely on its own as a products; product is 100% pure component)

1.3. Objectives

This main objective of this research is to develop a Mixed-Integer Linear program (MILP), whose solution will determine the optimal design of distillation sequences for producing olefins. The main variable in the proposed modeling approach are: (1) the flow rates of the material streams; (2) the selection of the process units to be selected and the interconnectivities among the selected units that give rise to their sequence. In order to achieve the main objective, the following sub-objectives are formed.

1. To consider a suitable superstructure representation for olefin production such as STN, SEN, and intermediate;

2. To derive a mathematical programming model with discrete and continuous variables to predict an optimum flow sheet design that includes linear mass balances and constraints for the selection of the alternative routes for the olefin production;
3. To solve the optimization model for optimal separation sequences for olefin production using modeling language interface GAMS (general algebraic modeling language);

1.4. Scope

The scope of the research is to formulate a mixed integer liner programming model (MILP)) for olefin production. The scope for final year project 1 (fypI) is to develop the suitable superstructure for olefin production, formulate the linear mass balance, and develop logical constraints. The scope for final year project II (fypII) is to model the MILP model in GAMS and validate the results obtained with literature review.

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CHAPTER 2

LITERATURE REVIEW

2.1 OLEFIN FEEDSTOCK

The typical feedstocks for petrochemical industry for olefin production are ethane, propane, naphtha and gas oil. Regardless of the feedstock, olefin production is a gigantic destroyer of energy, an enormous heat sink. Olefin production is very energy intensive (Hatch and Matar, 1981).

The gaseous feedstocks for ethylene production are ethane, propane, and *n*-butane, in various mixtures and proportions of these compounds (Hatch and Matar, 1981). The advantage of ethane as a feedstock is a high ultimate yield combined with a minimum of coproducts. The ultimate yields of ethylene is about 80% based on the ethane is being recycled to extinction (Hatch and Matar, 1981).For propane feedstock, it gives a lower ethylene yield and a larger quantity of coproducts than ethane feedstock (~~Figure~~ Table 1).

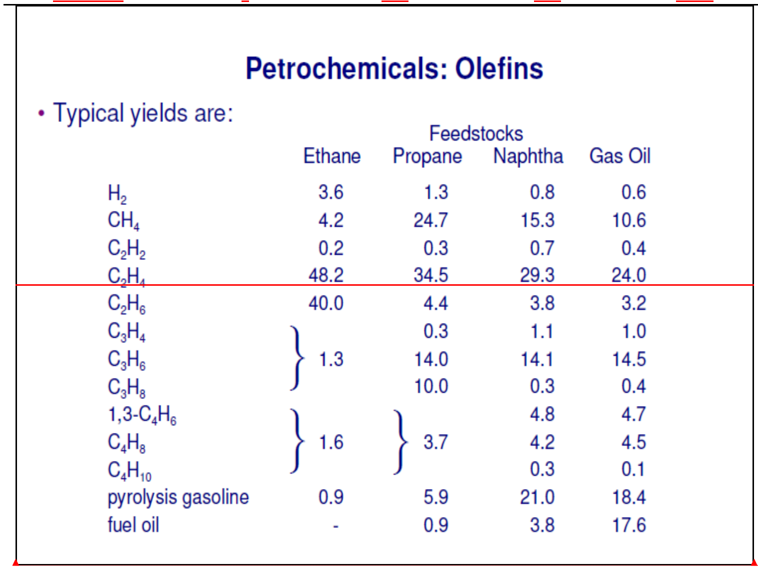
The major liquid feeds/feedstock for olefins production are light virgin naphtha, full range naphtha, reformer raffinate, atmospheric gas oil, vacuum gas oil, resids, and crude oil. The feedstock are usually cracked with lower residence times and higher temperatures and with higher steam dilution ratios than is used for gas feedstocks (Hatch and Matar, 1981). The advantage of naphtha over gas feestocks is the wider spectrum of coproducts (~~Figure~~ Table 1).The important olefins and aromatics used for production in chemical industry are ethylene, propylene, butadiene, BTX. Thus, we wish to obtain a variety of copoducts. ~~Figure~~ Table 1 shows that as feedstocks progress from ethane through heavier fractionation with lover H_2 content, the yield of ethylene is reduced and the variety of coproducts are increased.

Table 1 Typical yield of feedstocks in olefin production

Petrochemicals: Olefin

Typical yields are:

	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		0.3	1.1	1.0
C_3H_6	1.3	14.0	14.1	14.5
C_3H_8		10.0	0.3	0.4
1.3-C_4H_6			4.8	4.7
C_4H_8	1.6	3.7	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



Petrochemicals: Olefins

- Typical yields are:

	Feedstocks			
	Ethane	Propane	Naphtha	Gas Oil
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

~~(retype) Figure 1 Typical yield of feedstocks in olefin production~~

An olefins plant, which utilizes a liquid feedstock, requires an additional pyrolysis furnace for cracking coproduct ethane and propane and an effluent quench exchanger.

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This is followed by an oil quench and a primary fractionator for fuel oil separation. In contrast, a gas cracker requires a simple direct-contact water quench tower off the cracking unit. A liquid feed cracker also contains a propylene tower and a methylacetylene removal unit. A unit for first stage hydrotreating of pyrolysis gasoline may also be included (Hatch and Matar, 1981).

2.2 Petrochemical Industry in Malaysia

The availability of hydrocarbon feedstocks from indigenous oil and gas has led to the development of the petrochemical industry. the two ethane crackers in kertih which use ethane from the six GPPs in Kertih and Tok Arun provide feedstock for the polyethylene plants, acetic acid plant and DOW PETRONAS ethylene derivatives complex. Condensates from the GPPs also provide feedstock to the aromatic plant in Kertih for the production of paraxylene and benzene.

Propane from the GPPs is the raw material for the propane dehydrogenation plant in Gebeng. This provides feedstock to the polypropylene and MTBE plants and also to the BASF Petronas highly integrated propylene derivatives complex for the production of acrylics, oxo alcohols, butanediol, butylacrylates, plasticizers and tetrahydrofurane.

Titan’s integrated operation in Pasir Gudang-Tanjung Langsat, Johor includes a naphtha cracker which provides feedstock for its own production of polypropylene, polyethylene and aromatics. It also provides feedstock for the production of ethylene vinyl acetate (EVA). Naphtha is available from the petroleum refineries and Shell’s middle distillates synthesis (MDS) plant in Bintulu, Sarawak. However a large proportion of the naphtha requirement is still being imported.

Production of Petrochemical Feedstocks (as at January 2005)

Petrochemical Products	Capacity (mtpa)	Company/Refinery
Naphtha	2,380,000	• Petronas Penapisan (Terengganu) Sdn Bhd • Petronas Penapisan (Melaka) Sdn Bhd • Malaysia Refinery Company Sdn Bhd • Shell Refinery Company (FOM) Bhd • Esso (Malaysia) Bhd
Methane (sales gas)	2,000 mmscfd	• Petronas Gas Berhad
Olefins:		
Ethane	1,383,000	
Propane	1,799,000	
Butane	1,166,000	
Condensate	1,260,000	
Propane	148,400	• Malaysia LNG Tiga Sdn Bhd
Butane	273,900	
Liquefied Petroleum Gas (LPG)	137,700	
Ethylene	1,560,000	• Titan Petrochemical (M) Sdn Bhd • Ethylene Malaysia Sdn Bhd • Optimal Olefins (M) Sdn Bhd
Propylene	766,000	• Titan Petrochemical (M) Sdn Bhd • MTBE (M) Sdn Bhd • Optimal Olefins (M) Sdn Bhd
Benzene, Toulene and Xylene (BTX)	775,000	• Titan Petrochemical (M) Sdn Bhd • Aromatics Malaysia Sdn Bhd

Figure 1~~Figure 2~~ Production of Petrochemical Feedstock (as at January 2005) (MIDA, 2005)

2.3 OVERVIEW ON PROCESS DESCRIPTION OF NAPHTHA CRACKING

The optimization-based mathematical model for the integration of flow from a refinery to a petrochemical plant is based on a process flowsheet superstructure representation that embeds all possible alternatives for the design of an olefin plant.

2.3.1 CRACKING OR PYROLYSIS SECTION

The primary process step in producing olefins from hydrocarbon feeds is thermal cracking, usually referred to as pyrolysis. This process converts the feed to lower molecular weight hydrocarbons at relatively high temperature and low pressure. Light naphtha is supplied to the cracker plant from storage tank via pumps. Pyrolysis is the heart of steam cracker. The naphtha feed is first entered to the convection section, where preheated to 650°C with a series of heat exchanger at the convection section. The naphtha is then vaporized with superheated steam and is passed into long, narrow tubes, which are made of chromium nickel alloys (ren et al., 2006). Recycle ethane and propane streams are mixed in the gas feed header while recycle C4 (hydrocarbon with four carbon atoms) are mixed preferentially with the fresh naphtha in the liquid feed header. Any excess of C4 will go to the gas feed header.

The cracking reactions take place mainly in the radiant section of the furnace, where the naphtha is cracked into smaller molecules via a free radical mechanism in the absence of catalyst. The free radicals lead to the formation of light olefins in gaseous state. The tubes in the radiant section are externally heated to 750-900^{o}C (up to 1100^{o}C) by fuel oil or gas fired burners (Ren et al., 2006). Dilution steam is added to reduce the hydrocarbon partial pressure to promote the production of olefins and minimize the rate of coke deposition. Periodic decoking is required to remove coke which accumulates gradually in the radiant coils and quench exchangers. The furnaces will be steam or air decoked when the tube metal temperature approaches its design limit.

Depending on the severity, naphtha is cracked into smaller molecules via a free radical mechanism in the absence of catalyst. Thus, the olefins are in the gaseous state. After leaving the furnace, the hot gas mixture is subsequently quenched in the transfer line exchangers (TLE) to 550 – 650°C or lower to 400^{o}C (Ren et al., 2006). Super high pressure (SHP) steam is generated (500 °c and 105 kg/cm^{2}g) and is used in the turbine driver for the cracked gas compressor. Rapid cooling is necessary to avoid secondary reactions which convert valuable products to heavier materials that tend to cause fouling in the exchangers. The steam generation pressure is set so that the tube wall temperature is high enough to prevent condensation of hydrocarbon in the TLE's.

2.3.2 PRIMARY FRACTIONATION, COMPRESSION AND QUENCH SYSTEM

Primary fractionation applies to the liquid feedstock of naphtha and gas oil feed only. In the primary fractionation section, gasoline and fuel oil streams (rich in aromatics) are condensed and fractionated. While this liquid fraction is extracted, the gaseous fraction is desuperheated in the quench tower by a circulating oil or water stream. The gaseous fraction is then passed through four or five stages of gas compression with temperatures at approximately 15-100 ^{o}C, then cooling and finally cleanup to remove acid gases, carbon dioxide and water. Most of the dilution steam is condensed, recovered and recycled. Product of primary fractionation are fuel il and BTX or aromatic gasoline which consists benzene, toluene, and xylene. The problem faced with compression is fouling with cracked gas compressors and after coolers. The build–up of polymers on the rotor and internal will leads to energy losses as well as mechanical problems. Wash oil and water used to reduce fouling (Ren et al., 2006).

Furnace effluent gas is cooled further by direct contact with circulating quench oil and fractionated in a quench oil tower to remove the heavy fraction. This quench oil material is stripped to control flash point and sent to storage as fuel oil product. The overhead from the quench oil tower will enter the quench water tower. Most of the dilution steam condenses in this tower, along with a portion of the gasoline fraction.

2.3.3 CAUSTIC WASHING & DRYING

The caustic wash tower is installed to remove hydrogen sulphide, mercaptans, and carbon dioxide formed during the cracking process. These acid gases are removed from the cracked gas for the following purposes:

1. to meet product quality requirements on the ethylene and propylene products
2. to protect downstream catalytic operations, since some acid gas components are known to be catalyst poisons
3. to avoid corrosion
4. to avoid the possible formation of carbon dioxide ice within the cold process systems.

The caustic solution used in this process is caustic soda (sodium hydroxide). After four stages of compression, the acid gases of the cracked gas are removed by scrubbing the gas with circulating caustic solution in the caustic tower. The tower consists of three sections, only two of which provide the caustic scrubbing of the cracked gas. The middle and bottom sections are circulated with strong and weak caustic solutions, respectively. The top section is the water wash section, which washes the treated cracked gas to prevent caustic carryover into the downstream equipment.

Removal of acid gas at this point in the process allows all of the C4 and lighter hydrocarbons to be desulfurized together, eliminating the necessity to clean individual product streams. Overhead gas from the caustic tower is cooled with propylene refrigerant. The condensate is pumped forward to the high pressure (HP) depropanizer via the liquid dryer unit. Essentially, complete removal of water is necessary to prevent freeze-ups in subsequent low temperature equipment.

2.3.4 PRODUCT RECOVERY AND FRACTIONATION SECTON

This is essentially a separation process through distillation, refrigeration, and extraction. Equipment includes chilling trains and fractionation towers, which include refrigeration, demethanizer, deethanizer and others which shown in Figure 4.

i. Depropanizer

The dried gases are cooled and fed to the HP depropanizer, which separates the feed into an overhead vapor essentially free of C4 and heavier material and a bottoms product essentially free of C2 (hydrocarbon with two carbon atoms) and lighter material. Tower overhead vapor is compressed in the fifth stage of the cracked gas compressor. Net bottom flows to the low pressure (LP) depropanizer. The 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

Gas from the fifth stage of the cracked gas compressor is catalytically hydrogenated to remove acetylene. The reactor feed gas may either be cooled or heated, depending on the age and activity of the catalyst. Catalyst life is expected to be at least three years between regeneration. Three catalyst beds are used, with inter-cooling between beds to limit the temperature rise per bed. Essentially, all acetylene is converted to ethylene and ethane. Some of the methylacetylene and propadiene is converted to propylene. a spare reactor is not required because on-line regeneration is not required. Effluent from the reactor is cooled and dried in a secondary dryer to remove any trace quantities of water. Dried gas is cooled and partially condensed to provide reflux for the hp depropanizer.

iii. Demethanizer

The effluent gas from the hydrogenation reactor is chilled by exchange with ethane recycle and successively colder levels of propylene and ethylene refrigeration. Liquids separated in the chilling train are fed to appropriate trays in the demethanizer prefractionator and demethanizer, according to composition. 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. The demethanizer makes a sharp separation between methane and ethylene.

iv. Deethanizer & C2 splitter systems

The deethanizer separates the feed into C2 and C3. The net overhead, consisting principally of ethylene and ethane, is taken as a liquid to a C2 splitter, while the net bottom is fed to C3 hydrogenation. 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.

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. Ethane bottom from the splitter is pumped and vaporized by exchange with demethanizer feed, and recycled to the cracking furnaces.

v. C3 hydrogenation, C3 splitter, Debutanizers Systems

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.

Hydrogenated C3 are pumped to the C3 splitter which consists of two towers: a stripper and a rectifier. The overhead from the stripper is fed to the rectifier. Light ends, a result of the hydrogenation reaction, are removed in the pasteurizing section of the rectifier. Propylene is condensed and returned as reflux. Reflux for the stripper is obtained from the bottom of the rectifier. The rectifier overhead is condensed by cooling water. The polymer grade propylene product is taken off as a liquid side draw. A propane rich stream is removed as a vapor product from a location two trays above the bottom of the stripper to be recycle cracked in the furnaces. The net bottom liquid is recycled back to the LP depropanizer to remove any green oil produced in the C3 hydrogenation unit.

The debutanizer receives a liquid feed from the LP depropanizer bottom. A separation is made between C4 and C5 (hydrocarbon with five carbon atoms). The overhead is condensed against cooling water. LP steam provides reboiler heat. 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.

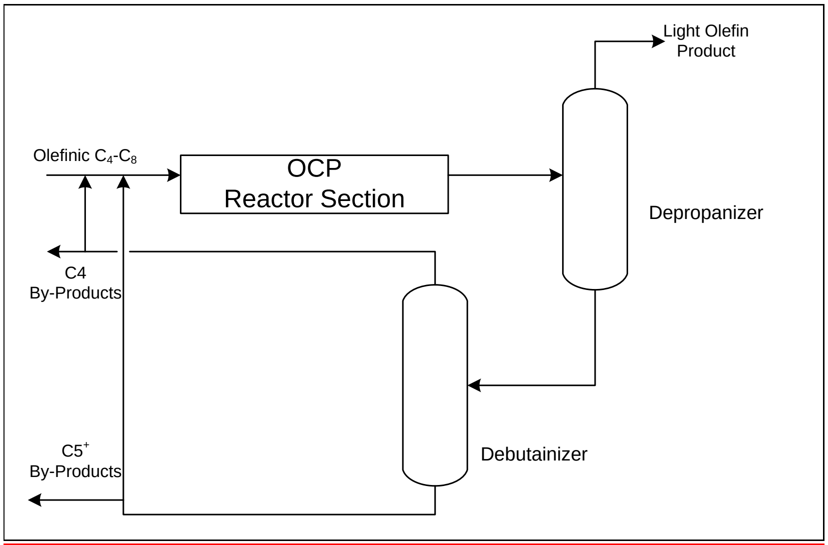
vi. C4 and Pyrolysis & Hydrogenation Unit

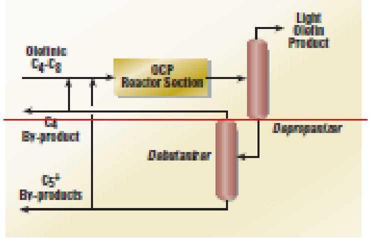
The C4 hydrogenation unit selectively converts butadiene to butenes using high purity hydrogen. The unit consists of a single fixed-bed catalytic reaction system. The C4 product stream is recycle cracked in the cracking furnaces.

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.

vii. Olefin Cracking Process

Based on UOP (2004), the Olefin Cracking process converts C_4 to C_8 olefins to propylene and ethylene at high propylene and ethylene ratio.See Figure ~~3~~2, the Olefin Cracking Process features fixed bed reactors operating at temperatures between 500 and 600 ^{0}C and pressures between1 to 5 bar gauge. The process utilizes a proprietary zeolitic catalyst and provides high yields of propylene. The catalyst minimizes the reactor size and operating costs by operating at high space velocities and high conversions and selectivities without requiring an inert diluent stream. A swing reactor system is used for catalyst regeneration. Separation facilities depend on how the unit is integrated into the processing system.





~~Figure 3~~ Figure 2 Description of Olefin Cracking Process

2.5 Overview of Process Description of Ethane Cracking

A typical ethane cracker has several identical pyrolysis furnaces in which fresh ethane feed and recycle ethane are cracked with steam as a diluent. The outlet temperature is usually in the 850 ^{o}C range. The furnace effluent is quenched in a heat exchanger and further cooled by direct contact in a water quench tower where the diluent steam is condensed. The water is recycled to the pyrolysis furnace. The cracked gas is compressed, acid constituents are removed, and the purified gas dried (Hatch and Matar, 1981).

Hydrogen and methane are removed from the pyrolysis products in the demethanizer, The product stream is hydrogenated to remove acetylene, or the acetylene is separated as a product. Ethylene is separated in the ethylene tower from the unreacted ethane and higher boiling products. The ethane is recycled to extinction. The other products are separated and either sold, burned as fuel, or absorbed into a refinery operation (Hatch and Matar, 1981).

The liquid feedstocks are usually cracked with lower residence times and higher temperatures and with higher steam ratios than is used for gas feedstocks. The reaction section of the plants is essentially same as with the gas feedstocks but the design of the convection and quenching section are different (Hatch & Matar, 1981). An olefin plant which utilizes a liquid feedstock requires an additional pyrolysis furnance for cracking co product ethane and propane and an effluent quench exchanger. This is followed by an oil quench and a primary fractionator for fuel oil separation. In contrast, a gas craker requires a simple direct-contact water quench tower off the cracking unit. A liquid feed cracker also contains a propylene tower and a methylacetylene removal unit. A unit for first stage hydrotreating of pyrolysis gasoline may be included (Hatch & Matar, 1981).

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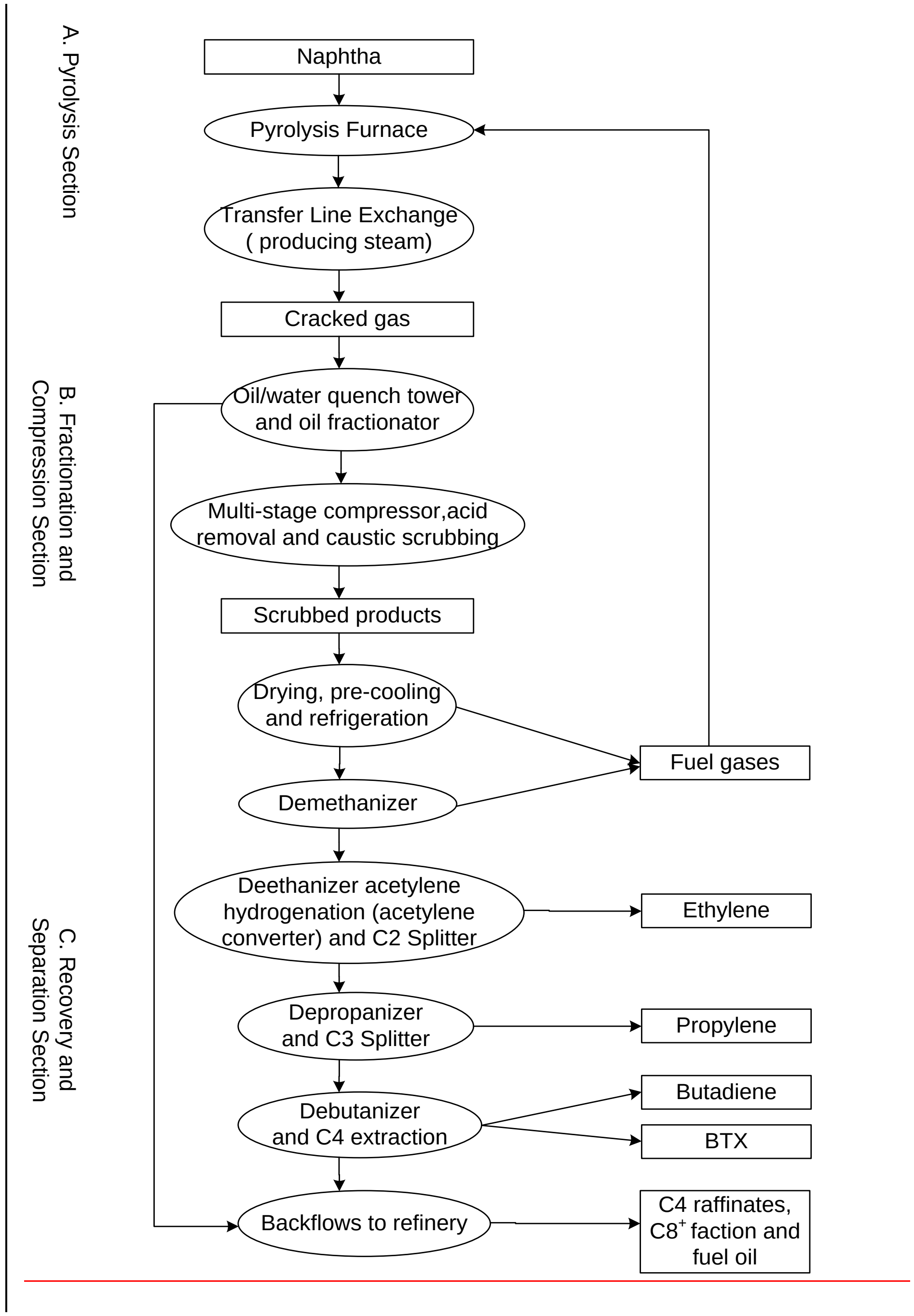
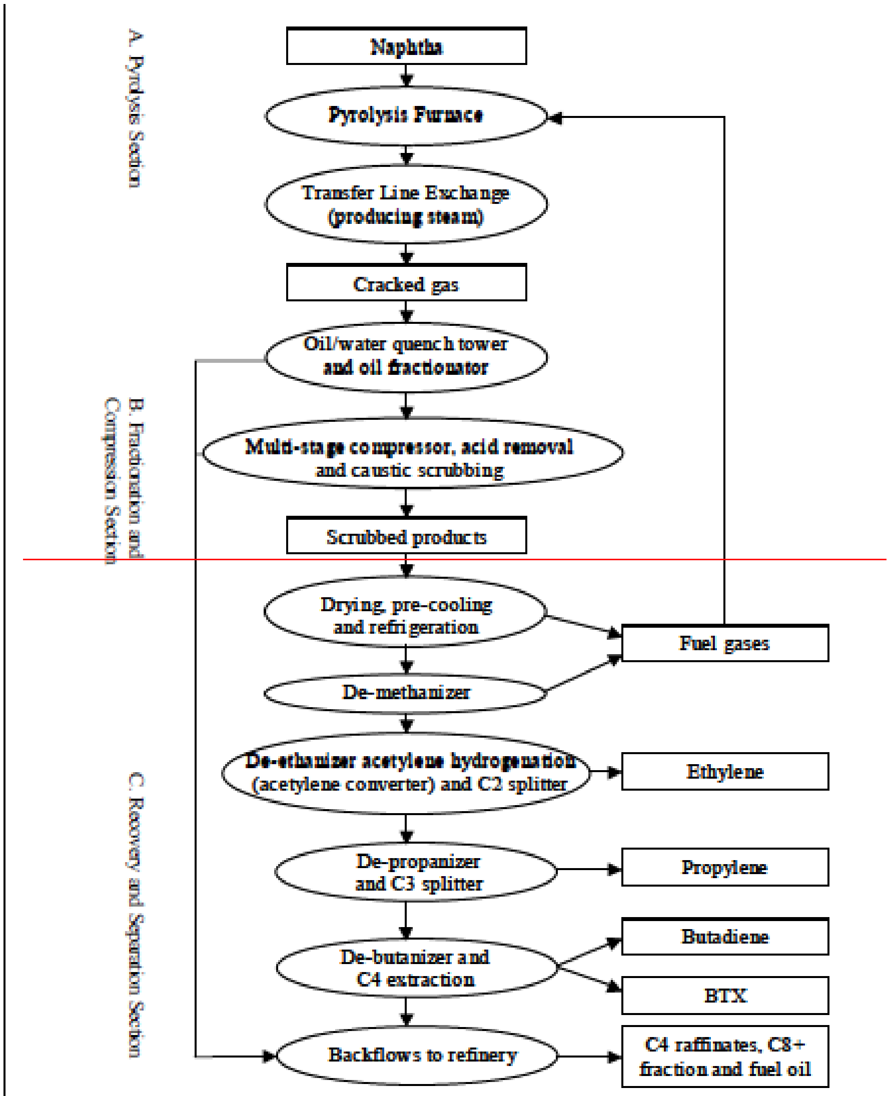

A. Pyrolysis Section
B. Fractionation and Compression Section
C. Recovery and Separation Section
Naphtha
Pyrolysis Furnace
Transfer Line Exchange (producing steam)
Cracked gas
Oil/water quench tower and oil fractionator
Multi-stage compressor,acid removal and caustic scrubbing
Scrubbed products
Drying, pre-cooling and refrigeration
Fuel gases
Demethanizer
Deethanizer acetylene hydrogenation (acetylene converter) and C2 Splitter
Ethylene
Depropanizer and C3 Splitter
Propylene
Debutanizer and C4 extraction
Butadiene
BTX
Backflows to refinery
C4 raffinates, C8+ faction and fuel oil



~~Figure 4~~Figure 3 A typical flow sheet of naphtha cracking plant (Ren,et al,2006)

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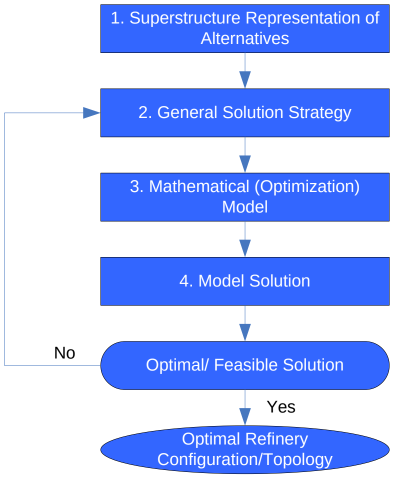
CHAPTER 3

Methodology

In general, the mathematical programming approach to process synthesis and design activities and problems consists of the following four major steps (Grossmann, 1990; Floudas, 1995, pp. 233.234; Novak et al., 1996):

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 (i.e. 1st stage, solve NLP (fix binary variables), 2nd stage, solve MILP using NLP solution).
3. Formulation or modeling 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.

The block diagram of the four major steps mentioned above is shown in Figure ~~5~~4.



~~Figure 5~~ Figure 4 Steps in mathematical programming approach to process synthesis and design problems (Grossman, 1990; Floudas, 1995; Novak et al., 1996)

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3.1 MILP Objective Function

In order to formulate a MILP program for this problem, it is important to devise an objective function which can be used to compare different alternatives. Thus, the objective function is to minimize the project cost, which is made up of capital expenses and operating expenses. This cost can be approximated by a function of the form of (1).

$$Cost = \sum_{k \in COL} \mathrm{CAPEX}_k y_k + \sum_{k \in COL} \mathrm{OPEX}_k F_k \qquad (1)$$

Where ~~FC = Fixed cost associated with the column~~
~~V = Slope of line relating the column cost~~
F_k = stream flow rate associated with the column, *k* with process unit *i*
CAPEX = Capital Expenses
OPEX = Operating Expenses
y_k= Binary variable denoting the existence or nonexistence of column *k*

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This objective function is subject to two types of constraints. Material balance constraints describe the permissible routes by which material may flow from one column in the superstructure to another. The second type of constraints which is integrality constraints, ensure consistency between the continuous variables and binary variables. The data of installed capital cost and operating cost are taken from Meyers (2005)(see Table ~~1~~2).

Table 2~~21~~ Ethylene Production Cost Components[a,b]

Location	N.E Asia/ W.Europe	Middle East	United States
Feedstock	Naphtha	Ethane	Ethane
Feedstock Cost (\$/t feed)	320[c]	62[d]	317[e]
Net Feedstock Cost[f] (\$/t C_2H_4)	55	68	266
Energy Cost (\$/ t C_2H_4)	194	16	140
Fixed Cost[g] (\$/t C_2H_4)	66	56	51
Total Production Cost (\$/t C_2H_4)	315	140	457
Contract sales Price (\$/t C_2H_4)		650-700	

[a] Amortazation costs for capital investment are excluded.

[b] Cost basis: first quarter 2004

[c] N.E.Asia/W.Europe naphtha cost = approx. $37.5/bbl (130% crude price)

[d] Middle East ethane cost = $1.25/MMBtu

[e] United States ethane cost = $ 5.45/MMBtu natural gas + $1.0/MMBtu extraction cost

[f] Net feedstock cost = feedstock cost – price of total nonethylene co-products

[g] Fixed cost include labour, supervision, maintenance, insurance , overhead.

3.2 Logical Constraints

The propose procedure to develop the logical relationships in the model is as below:

1. Associate Boolean Variables with every note in the model.

Boolean variables Y is used to represent the existence of all the units (U_n) in the superstructure while Z is used to represents the splitters, mixer, sources and sinks.

a. Mixer:
   Mixes two or more streams, no other unit operation is involved
b. Splitter:
   Splits a stream into multiple streams, no other unit operation is involved.
c. Unit:
   Including units that perform a change in compositions, pressure and temperature in the output streams, e.g. reactor, distillation columns.
d. Sources and sinks:
   Inlet and outlet of the process flowsheet.

2. Develop relationships between Boolean variables (Figure ~~6~~5).

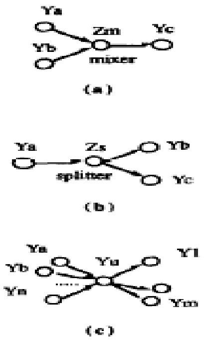

Figure 5 ~~Figure 6~~ Nodes in the graph of a superstructure: (a) mixer; (b) splitter; and (c) Un component.

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a. Mixer:

$$Z_m \Rightarrow Y_a \vee Y_b$$
$$Z_m \Rightarrow Y_c$$

If $Y_a \vee Y_b \Rightarrow Z_m$ and $Y_c \Rightarrow Z_m$ are also valid, then the relations can be written as $Y_a \vee Y_b \Leftrightarrow Z_m$ and $Y_c \Leftrightarrow Z_m$, respectively.

b. Splitter:

$$Z_s \Rightarrow Y_a$$
$$Z_s \Rightarrow Y_b \vee Y_c$$

If $Y_a \Rightarrow Z_s$ and $Y_b \vee Y_c \Rightarrow Z_s$ are also valid, the relations can be written as $Z_s \Leftrightarrow Y_a$ and $Z_s \Leftrightarrow Y_b \vee Y_c$ respectively.

c. Units $u \in U_n$:

$$Y_u \Rightarrow Y_a \wedge Y_b ... \wedge Y_n$$
$$Y_u \Rightarrow Y_a \wedge Y_b ... \wedge Y_m$$

3. User specification

User specifications limit on the unit selection and also take into account of the availability of the feed streams. The basic relation of Boolean Variable, Y with linear inequalities of binary variable, y is given in Table ~~2~~3.

Table 3~~32~~ Constraint representation of logical relations as algebraic linear inequalities (Adapted from Raman and Grossmann (1991) and Williams (1999))

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		$y_q = y_1 + y_2 + \cdots + y_r$

The systematic procedure to convert a logical expression into its corresponding conjunctive normal consists of applying the following three steps to each logical proposition (Raman and Grossmann, 1991):

1. replace the implication by its equivalent disjunction:

$$Y_1 \Rightarrow Y_2 \Leftrightarrow \neg Y_1 \vee Y_2;$$

2. move the negation inward by applying DeMorgan's Theorem:

$$\neg\left(Y_1 \wedge Y_2\right) \Leftrightarrow \neg Y_1 \vee \neg Y_2;$$
$$\neg\left(Y_1 \vee Y_2\right) \Leftrightarrow \neg Y_1 \wedge \neg Y_2;$$

3. recursively distribute the "OR" over the "AND" by using the following equivalence:

$$\left(Y_1 \wedge Y_2\right) \vee Y_3 \Leftrightarrow \left(Y_1 \vee Y_3\right) \wedge \left(Y_2 \vee Y_3\right)$$

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~~3.3 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 general formulation of the big-*M* logical constraints is given by:~~

~~$F_k \le M_k y_k$ (2)~~

~~where F_k = total flowrate of an input stream for process unit *k* in kg/day,~~
~~M_k = maximum capacity of process unit *k*~~
~~y_k = existence or non existence of process unit *k*.~~

~~We could see that when $y_i = 0$ (unit does not exist), then the constraint (2) becomes:~~

~~$F_k \le 0$ (3)~~

~~but flowrate variables are either zero or takes on positive values, so equation (3) becomes $F_k = 0$, which stipulates the condition of zero input flowrate into a non-existing unit. When $y_k = 1$ (unit exists), then the constraint (2) becomes:~~

~~$F_k \le M_k$ (4)~~

~~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.~~

~~For example equation (5), if the maximum capacity of a distillation column is equals to 100 m^3, then the big-M logical constraint for that unit becomes~~

~~$F_k \le \left(100\ \mathrm{m}^3\right) y_k$ (5)~~

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~~This constraint (4) is usually written for the input flowrate because it can be related to the output flowrates through the material balances.~~

~~The big-*M* logical constraints are also sometimes termed as switching constraints in the literature (Rardin, 1998, p. 558). 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 $_i \leq M_i z_i$ 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, *ta*ken to be an arbitrarily large number, 1000, which it acts as an upper bound for the corresponding feed flow rate of the initial mixture.~~

~~3.4 Linear Material Balances~~

~~According M.J.Andrecovich and A.W. Westerbeurg (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 equation (6)~~

$$D_k = \xi_D F_k$$

$$B_k = \xi_B F_k = (1-\xi_D) F_k$$ ~~(6)~~

~~Where ξ_D is the split fraction of the feed to column,k which leaves in the distillate and ξ_B is the split fraction that leaves in the bottoms. 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. That is~~

$$\sum_{k \in PS_m} \xi_k F_k - \sum_{k \in FS_m} F_k = 0 \qquad m \in IP$$ ~~(7)~~

~~Where PS_m is the set of all columns which produce a given intermediate product *m* as distillate or bottoms, FS_m is the set of all columns having intermediate product *m* as~~

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~~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 (7) is written for each intermediate product.~~

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

$$\sum_{k \in FS_F} F_k = F_{TOT} \qquad (8)$$

~~Refer to equation (8), the total feed to the system must equal the sum of the feeds to all columns which process some portion of the feed stream.~~

CHAPTER 4

OPTIMIZATION MODEL FORMULATION

Due to time constraint, the project scope is narrowed down to the separation subsystem of the superstructure. An alternative superstructure representation that is proposed by Caballero and Grossmann (1999), termed simply as the intermediate representation is employed to represent the separation subsystem. In this project, intermediate superstructure representation was used for the distillation sequencing for olefin production.

4.1 Intermediate Superstructure Representation

Intermediate representation possesses the characteristics between the state–task network (STN) and the state–equipment network (SEN) superstructure representation.

For STN, the tasks and states are defined while the equipment assignment is generally unknown (See Figure 6~~7~~).For SEN, tasks and equipment are defined while the assignment of tasks to equipment must be determined (Yeomans and Grossmann, 1999)(See Figure ~~8~~7).In distillation sequencing problem, both SEN and STN are extreme cases because the number of columns is equal to the number of tasks for STN while the number of columns in SEN is the minimum necessary to perform the separation. Table ~~3~~ 4 shows the comparison between STN and SEN.

Referring to Figure 8~~9~~, the number of columns in intermediate representation is in between these two extreme separations/cases (Caballero and Grossmann, 1999).Hence,

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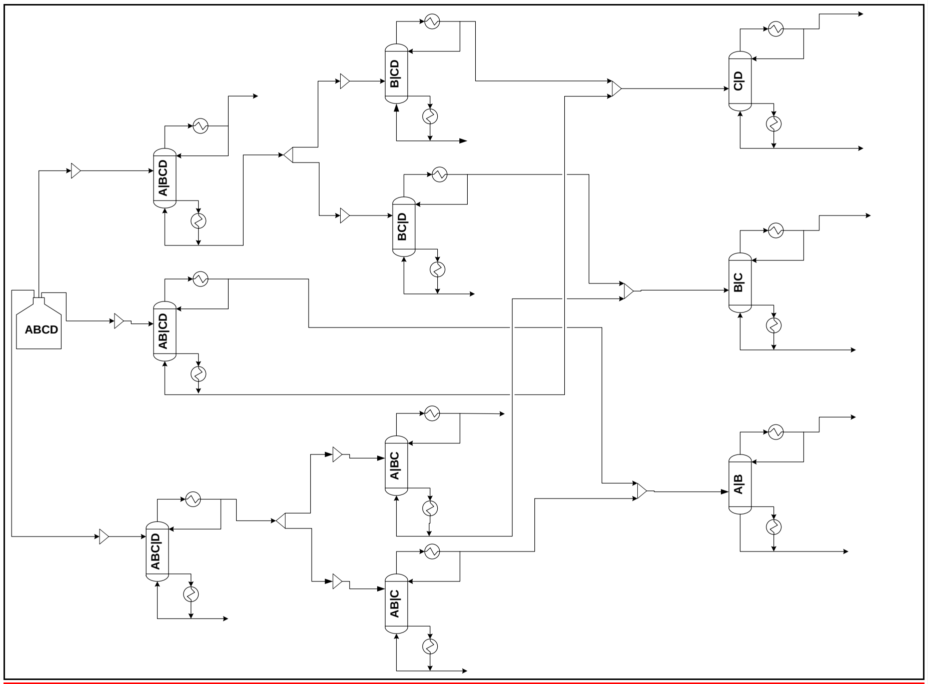
Formatted: Justified, Indent: Left: 1.5", First line: 0.5", Line spacing: 1.5 lines intermediate representation superstructure will involve less number of equations compared to STN representation superstructure. Intermediate representation has shown a good performance in reaching the global optimal solution (Caballero and Grossmann, 1999). Note also that for intermediate representation, both mixers and splitters are “single choice”, that is, only one input stream from the mixer or only one output stream from the splitter takes a non-zero value (i.e., a value different from zero). A contribution of this work pertaining to systematic superstructure generation is on how we demonstrate that the intermediate representation of Caballero and Grossmann (199) can be readily and conveniently extended to include the representation of reactors (in this case, the catalytic hydrogenation reactor, the methyl acetylene and propadiene reactor (MAPD), the C_4 hydrogenation reactor, and the gasoline hydrogenation reactor (which is basically a hydrotreater).



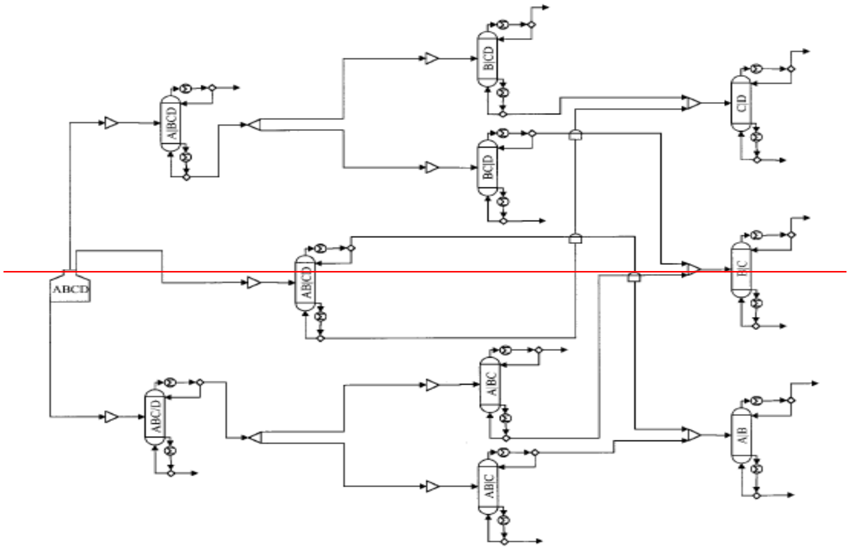


Figure 6~~7~~ STN Representation for a mixture of four components (Caballero & Grossmann, 1999)

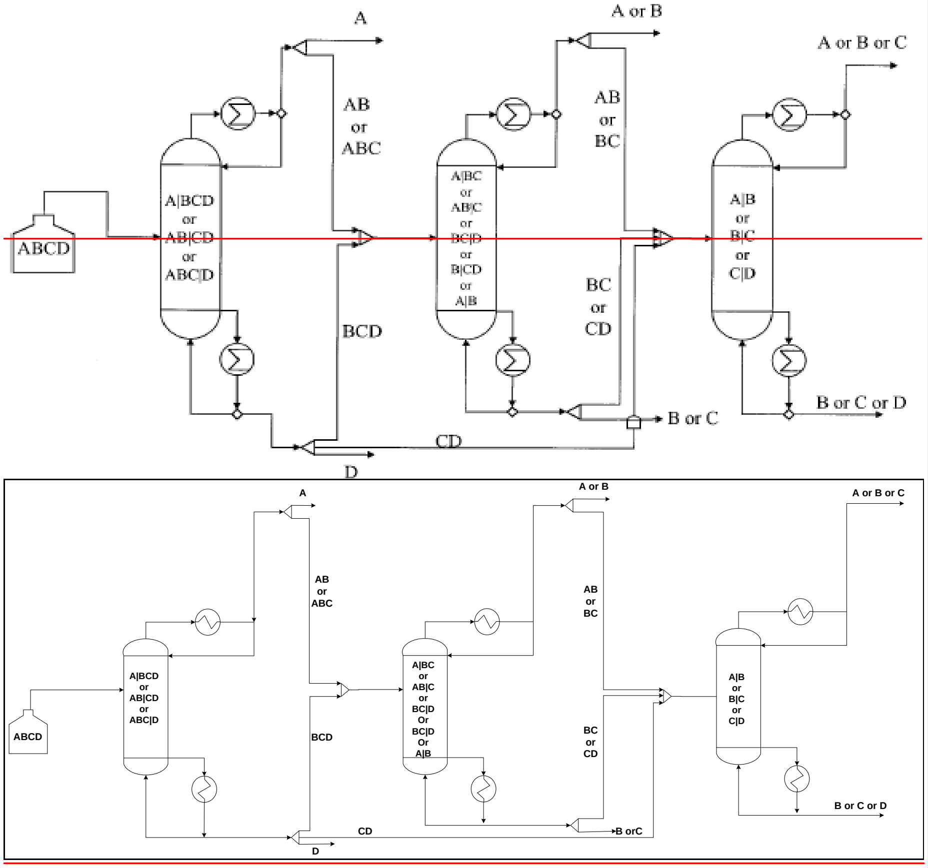


Figure ~~8~~ 7 SEN Representation for a mixture of four components (Caballero & Grossmann, 1999)

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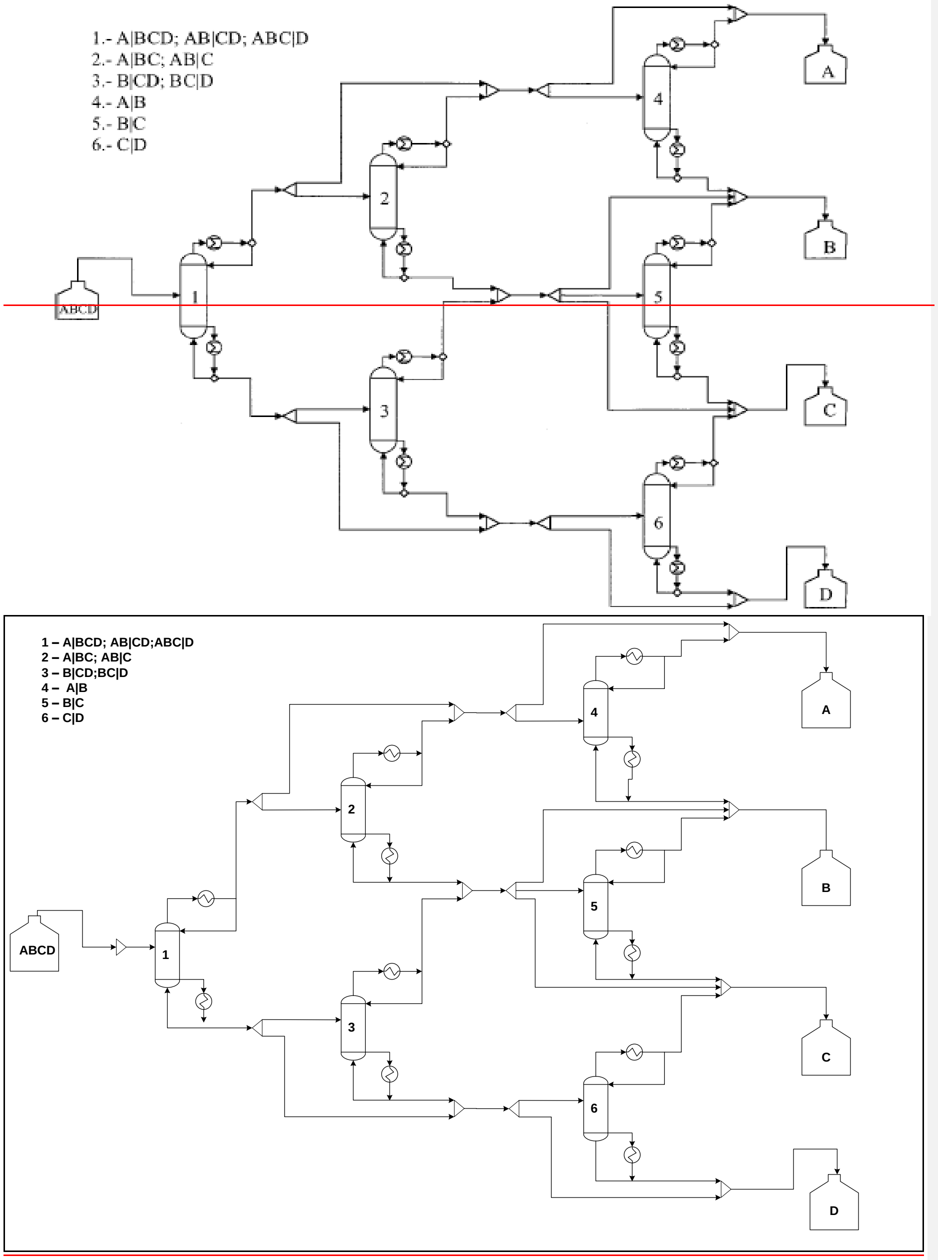
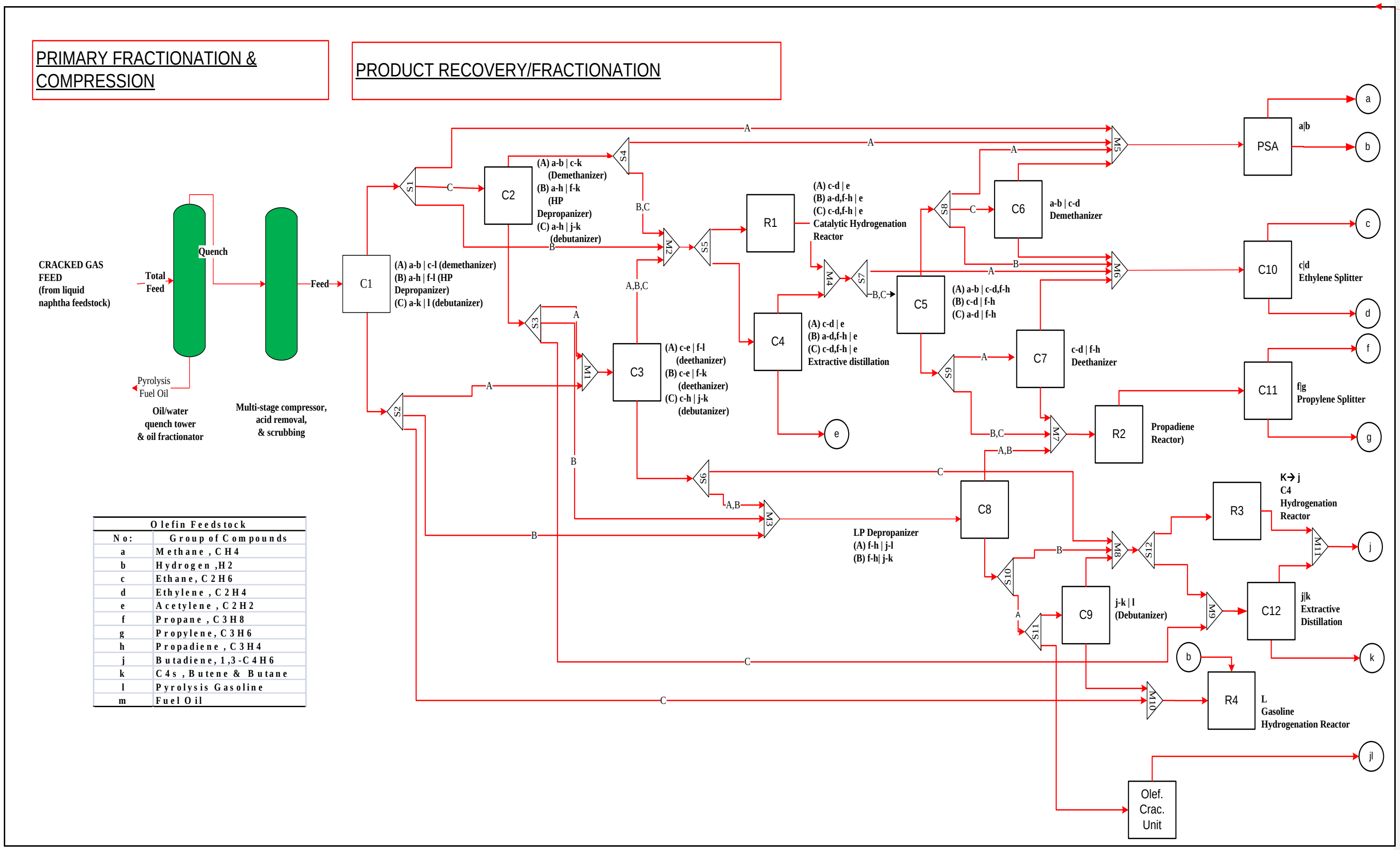


Figure ~~9~~ 8 Intermediate Representation for a mixture of four components(Caballero & Grossmann, 1999)

Table 44~~3~~ Comparison between STN and SEN

	STN	SEN
Characteristic	Concerned with the selection of tasks, leaving the equipment assignment (or selection) to a second stage	Concerned with the selection of equipment, leaving the selection (or assignment) of tasks to a second stage
Number of Columns	No. of columns = no. of tasks	No. of columns = minimum necessary to perform the separation (in the case that we are considering (N – 1) columns))
Difference	One task one equipment (OTOE) Each task is assigned to a single equipment unit. If a task can be executed by two different equipments, the tasks will have to be redefined to distinguish one from the other.	Tradeoff between the smaller combinatorial problem for equipment selection and the increasing problem complexity in the state definition



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

Figure ~~10~~9 Intermediate Representation of Distillation Sequencing for Olefin Production

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Figure 9 shows the intermediate representation of distillation sequencing for olefin production. The project scope is narrowed down to the product recovery or fractionation section. There are a few alternatives involved in the superstructure.

1. The first unit C1 consider different cuts :
   - Demethanizer – remove the light end first
   - HP depropanizer – use when the propane and heavier are main cracked feed.
   - Debutainzer – employs indirect sequence.

2. Different method to remove/separate acetylene from the stream:
   - Extractive distillation (task C4)
   - Catalytic hydrogenation reactor/ acetylene reactor (task R1) – improve the quality of specific product, e.g. upgrade the chemical grade ethylene to polymer grade ethylene.

3. Different method to remove /separate butadiene from mixed C4s mixture
   - Extractive distillation (task C12)
   - Catalytic hydrogenation reactor (task R3) – covert the butane and butane into butadiene.

4. ATOFINA/UOP Olefin Cracking Process (UOP, 2004) can be used to convert the heavy end product C4 to C8 olefin to propylene and ethylene at high propylene to ethylene ratio.
   - When integrated naphtha steam cracker the yield of propylene is increased dramatically for the same total naphtha flowrate.

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~~4.3~~4.2 Linear Material Balances

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According Andrecovich and 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 equation (2)

$$\begin{aligned} D_k &= \xi_D F_k \\ B_k &= \xi_B F_k = (1-\xi_D) F_k \end{aligned} \qquad (2)$$

Where ξ_D is the split fraction of the feed to column,k which leaves in the distillate and ξ_B is the split fraction that leaves in the bottoms. 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. That is

$$\sum_{k \in PS_m} \xi_k F_k - \sum_{k \in FS_m} F_k = 0 \qquad m \in IP \qquad (3)$$

Where PS_m is the set of all columns which produce a given intermediate product *m* as distillate or bottoms, FS_m is the set of all columns having intermediate product *m* 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 (3) is written for each intermediate product.

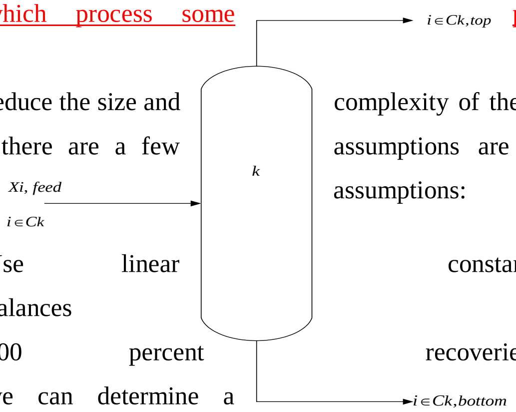
A similar expression is necessary for the feed to the distillation system:

$$\sum_{k \in FS_F} F_k = F_{TOT} \qquad (4)$$

Refer to equation (4), the total feed to the system must equal the sum of the feeds to all columns which 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:

a. Use linear constant-yield material balances
b. 100 percent 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 (~~9~~5) procedure to obtain the split fractions is as follows (Figure ~~11~~10):

$$\xi_{k,\mathrm{top}} = \frac{\sum_{i \in Ck,top} Xi,\ feed}{\sum_{i \in Ck,} Xi}$$

$$\xi_{k,bottom} = \frac{\sum_{i \in Ck,bottom} Xi,\ feed}{\sum_{i \in Ck,} Xi} \qquad (~~9~~5)$$

~~W~~where $Xi,\ feed$ = mole fraction of component *i* in the initial mixture,
Ck = set of component in the feed
Ck,top = set of components in the top or overhead,
$Ck,bottom$ = set of components in the bottom of column *k*

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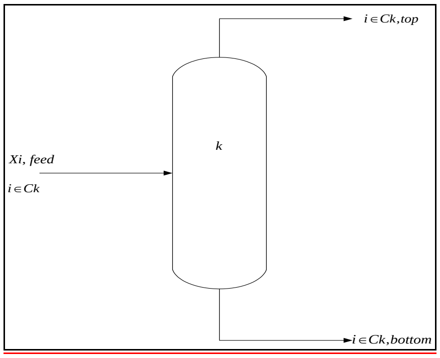

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Figure 5~~511~~ Module for total flow with sharp split

As an example, consider the mass compositions from University of Manchester's Centre for Process Integration (2005), the corresponding split fraction are shown in Table ~~4~~5.

Table 5~~54~~Split fraction based on mass composition from University Manchester's Centre for Process Integration (2005)

Split fraction based on mass composition from University of Manchester's Centre for Process Integration (2005)		
$\xi_{TotalFeed}^{a-l} = 0.9618$	$\xi_{C3a}^{c-e} = 0.4246$	$\xi_{C4a}^{c-d} = 0.9793$
$\xi_{TotalFeed}^{m} = 0.0382$	$\xi_{C3a}^{f-l} = 0.5754$	$\xi_{C4a}^{e} = 0.0207$
$\xi_{C1a}^{a-b} = 0.1682$	$\xi_{C3b}^{c-e} = 0.5768$	$\xi_{C4b}^{ad-fh} = 0.9893$
$\xi_{C1a}^{c-l} = 0.8318$	$\xi_{C3b}^{f-k} = 0.4232$	$\xi_{C4b}^{e} = 0.0107$
$\xi_{C1b}^{a-h} = 0.7387$	$\xi_{C3c}^{c-h} = 0.8413$	$\xi_{C4c}^{cd-fh} = 0.9858$
$\xi_{C1b}^{f-l} = 0.2613$	$\xi_{C3c}^{j-k} = 0.1587$	$\xi_{C4c}^{e} = 0.0142$
$\xi_{C1c}^{a-k} = 0.7806$	$\xi_{R1a}^{c-d} = 0.9793$	$\xi_{C5a}^{a-b} = 0.2488$
$\xi_{C1c}^{l} = 0.2194$	$\xi_{R1a}^{e} = 0.0207$	$\xi_{C5a}^{cd-fh} = 0.7512$
$\xi_{C2a}^{a-b} = 0.2155$	$\xi_{R1b}^{ad-fh} = 0.9893$	$\xi_{C5b}^{c-d} = 0.6811$
$\xi_{C2a}^{c-k} = 0.7845$	$\xi_{R1b}^{e} = 0.0107$	$\xi_{C5b}^{f-h} = 0.3189$

$\xi^{a-h}_{C2b} = 0.8632$	$\xi^{cd-fh}_{R1c} = 0.9858$	$\xi^{a-d}_{C5c} = 0.7604$
$\xi^{f-k}_{C2b} = 0.1368$	$\xi^{e}_{R1c} = 0.0142$	$\xi^{f-h}_{C5c} = 0.2396$
$\xi^{a-h}_{C2c} = 0.8755$	$\xi^{a-b}_{C6} = 0.3272$	$\xi^{c-d}_{C7} = 0.6811$
$\xi^{j-k}_{C2c} = 0.1245$	$\xi^{c-d}_{C6} = 0.6728$	$\xi^{f-h}_{C7} = 0.3189$
$\xi^{f-h}_{C8a} = 0.3384$	$\xi^{f-h}_{C8b} = 0.6250$	$\xi^{j-k}_{C9} = 0.3069$
$\xi^{j-l}_{C8a} = 0.6616$	$\xi^{j-k}_{C8b} = 0.3750$	$\xi^{j-k}_{C9} = 0.6931$

For initial node in the network we have Equation (~~10~~6),

$$\xi^{a-l}_{\text{TotalFeed}} F_{\text{Quench}} + \xi^{m}_{\text{TotalFeed}} F_{\text{Oil}} = \text{TOTFEED}$$
(~~10~~6)

~~$\xi^{a-l}_{\text{TotalFeed}} F_{\text{Quench}} + \xi^{m}_{\text{TotalFeed}} F_{\text{Oil}} = \text{TOTFEED}$~~

~~(10)~~

For the remaining nodes in the network, mass balances for each intermediate product are~~was~~ considered. Based on the split fractions of recoveries~~y~~ ~~sections~~ calculated~~given~~ in Table ~~4~~5, the mass balances for each intermediate product is as listed in ~~follows(~~Table ~~5~~6, as obtained from the following general constraint:~~):~~

$$\sum_{k \in PS_m} \xi_k F_k - \sum_{k \in FS_m} F_k = 0 \qquad m \in IP$$
(~~10~~3)

where PS_m is the set of all columns that produce a given intermediate product m as distillate or bottoms, FS_m is the set of all columns having intermediate product m as feed, and IP is the set of all intermediate products.

Table 6~~65~~ Mass balance for each intermediate product

Mass balances for each intermediate product
1. Intermediate (a-b) which is produced in C1a, C2a, C6 and C5a and directed to PSA.

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$$\xi_{C1a}^{a-b}F_{C1a}+\xi_{C2a}^{a-b}F_{C2a}+\xi_{C6}^{a-b}F_{C6}+\xi_{C5a}^{a-b}F_{C5a}-F_{PSA}=0$$

2. Intermediate (c-l) which is produced in C1a and directed to C3a.

$$\xi_{C1a}^{c-l}F_{C1a}-F_{C3a}=0$$

3. Intermediate (a-h) which is produced in C1b,C2b and C2c and directed to R1b and C4b.

$$\xi_{C1b}^{a-h}F_{C1b}+\xi_{C2b}^{a-h}F_{C2b}+\xi_{C2c}^{a-h}F_{C2c}-F_{R1b}-F_{C4b}=0$$

4. Intermediate (f-l) which is produced in C1b and C3a and directed to C8a.

$$\xi_{C1b}^{f-l}F_{C1b}+\xi_{C3a}^{f-l}F_{C3a}-F_{C8a}=0$$

5. Intermediate (a-k) which is produced in C1c and directed to C2a, C2b and C2c.

$$\xi_{C1c}^{a-k}F_{C1c}-F_{C2a}-F_{C2b}-F_{C2c}=0$$

6. Intermediate (l) which is produced in C1c and C9 and directed to R4.

$$\xi_{C1c}^{l}F_{C1c}+\xi_{C9}^{l}F_{C9}-F_{R4}=0$$

7. Intermediate (c-k) which is produced in C2a and directed to C3b and C3c

$$\xi_{C2a}^{c-k}F_{C2a}-F_{C3b}-F_{C3c}=0$$

8. Intermediate (f-k) which is produced in C2b and C3b and directed to C8b

$$\xi_{C2b}^{f-k}F_{C2b}+\xi_{C3b}^{f-k}F_{C3b}-F_{C8b}=0$$

9. Intermediate (j-k) which is produced in C2c, C3c, C8b, and C9 and directed to C12

$$\xi_{C2c}^{j-k}F_{C2c}+\xi_{C3c}^{j-k}F_{C3c}+\xi_{C8b}^{j-k}F_{C8b}+\xi_{C9}^{j-k}F_{C9}-F_{C12}=0$$

10. Intermediate (c-e) which is produced in C3a and C3b and directed to R1a and C4a

$$\xi_{C3a}^{c-e}F_{C3a}+\xi_{C3b}^{c-e}F_{C3b}-F_{R1a}-F_{C4a}=0$$

11. Intermediate (c-h) which is produced in C3c and directed to R1c and C4c

$$\xi_{C3c}^{c-h}F_{C3c}-F_{R1c}-F_{C4c}=0$$

12. Intermediate (c-d) which is produced in R1a,C4a,C6,C7 and C5b and C3b and directed to C10

$$\xi_{R1a}^{c-d}F_{R1a}+\xi_{C4a}^{c-d}F_{C4a}+\xi_{C6}^{c-d}F_{C6}+\xi_{C7}^{c-d}F_{C7}+\xi_{C5b}^{c-d}F_{C5b}-F_{C10}=0$$

13. Intermediate (ad-fh) which is produced in R1b and C4b and C3b and directed to C5a and C5c

$$\xi_{R1b}^{ad-fh}F_{R1b}+\xi_{C4b}^{ad-fh}F_{C4b}-F_{C5a}-F_{C5c}=0$$

14. Intermediate (cd-fh) which is produced in R1c, C4c and C5a and directed to C7.

$$\xi_{R1c}^{cd-fh}F_{R1c}+\xi_{C4c}^{cd-fh}F_{C4c}+\xi_{C5a}^{cd-fh}F_{C5a}-F_{C7}=0$$

15. Intermediate (a-d) which is produced in C5c and directed to C6

$$\xi_{C5c}^{a-d}F_{C5c}-F_{C6}=0$$

16. Intermediate (f-h) which is produced in C5b, C5c,C7,C8a and C8b and directed to R2

$$\xi_{C5b}^{f-h}F_{C5b}+\xi_{C5c}^{f-h}F_{C5c}+\xi_{C7}^{f-h}F_{C7}+\xi_{C8a}^{f-h}F_{C8a}+\xi_{C8b}^{f-h}F_{C8b}-F_{R2}=0$$

17. Intermediate (j-l) which is produced in C8a and directed to C9 and OCU

$$\xi_{C8a}^{j-l} F_{C8a} - F_{C9} - F_{OCU} = 0$$

4.~~2~~3 Logical Constraints on Design Specifications, Interconnectivity Relationships and Switching Constraints

Logical constraints are developed for the intermediate representation superstructure in Figure ~~10~~9 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 logical constraints and switching constraints are also developed for the entire Intermediate superstructure representation and they are included in Table ~~6~~7 and Table ~~7~~8.

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

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;

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;

F_j: flow rate variable of a state (or material stream) *j*; and

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, we have found it desirable to only consider the selection of the process units; thus, we have omitted the modeling of the stream selection in the logical constraints. The same reason has been stressed in Raman and Grossmann (1993), which goes on to assert that this is indeed commonly the case in problems of similar nature.

Tables ~~6~~ 7 and ~~7~~8, present the logical constraints on design specifications and logical constraints on interconnectivity relationships (structural specifications) respectively for the feed and cracking subsystem. Logical constraints on design specifications are needed especially for distillation columns (and reactors) in which selection of a single task that takes place in the column needs to be made.

Table 7~~76~~ **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), HP depropanizer (C2b), and debutanizer (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)	$Y_{a-b\|c-k}^{\mathrm{C2a}} \vee Y_{a-i\|f-k}^{\mathrm{C2b}} \vee Y_{a-i\|j-k}^{\mathrm{C2c}}$	$y_{a-b\|c-k}^{\mathrm{C2a}} + y_{a-i\|f-k}^{\mathrm{C2b}} + y_{a-i\|j-k}^{\mathrm{C2c}} \le 1$
DS3	Select only one or none of the deethanizer (C3a, C3b) or debutanizer (C3c).	$Y_{c-e\|f-l}^{C3a} \vee Y_{c-e\|f-k}^{C3b} \vee Y_{c-i\|j-k}^{C3c}$	$y_{c-e\|f-l}^{C3a} + y_{c-e\|f-k}^{C3b} + y_{c-i\|j-k}^{C3c} \le 1$
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)	$Y_{c-d\|e}^{R1a} \vee Y_{a-d,f-h\|e}^{R1b} \vee Y_{c-d,f-h\|e}^{R1c}$	$y_{c-d\|e}^{R1a} + y_{a-d,f-h\|e}^{R1b} + y_{c-d,f-h\|e}^{R1c} \le 1$
DS5	Extractive distillation column (C4) separates acetylene from the other components. As in previous, components entering C4 depend on the unit selected upstream.	$Y_{c-d\|e}^{C4a} \vee Y_{a-d,f-h\|e}^{C4b} \vee Y_{c-d,f-h\|e}^{C4c}$	$y_{c-d\|e}^{C4a} + y_{a-d,f-h\|e}^{C4b} + y_{c-d,f-h\|e}^{C4c} \le 1$
DS6	At most two of the tasks for similar categories of tasks involving the catalytic reactor R1 or column C4 can be selected		$y_{c-d\|e}^{R1a} + y_{c-d\|e}^{C4a} \le 2$ $y_{a-d,f-h\|e}^{R1b} + y_{a-d,f-h\|e}^{C4b} \le 2$ $y_{c-d,f-h\|e}^{R1c} + y_{c-d,f-h\|e}^{C4c} \le 2$
DS7	Select at most one from among demethanizer (C5a), deethanizer (C5b), and depropanizer (C5c).		$y_{a-b\|c-d,f-h}^{C5a} + y_{c-d\|f-h}^{C5b} + y_{a-d\|f-h}^{C5c} \le 1$
DS8	Select only one or none from among LP depropanizer (C8a) and C8b	$Y_{f-h\|j-l}^{C8a} \vee Y_{f-h\|j-k}^{C8b}$	$y_{f-h\|j-l}^{C8a} + y_{f-h\|j-k}^{C8b} \le 1$
DS9	At most two tasks can be selected between C4 hydrogenation reactor R3 and extractive distillation column C12		$y_{j\|k}^{R3} + y_{j\|k}^{C12} \le 2$

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The logical constraints on structural specifications are categorized into~~to~~ two groups or ~~/~~sections~~ are categorized into~~:

(1) l~~L~~ogical constraints on structural specifications that involve the overhead and bottom products (Table ~~7a~~8a);

(2) l~~L~~ogical constraints on structural specifications that involve the feed or ~~/~~inlet to the columns (Table 8~~7~~b)
, which is similar to the constraints on sequence of task of columns as employed by~~(refer to~~ Floudas and Paules (1988).~~, p. 538)~~

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Table 8~~87~~(a) Logical constraints on structural specifications for interconnectivity relationships for the separation subsystem using intermediate representation which involve the overhead and bottom products

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Logic proposition on structural specification	Algebraic constraint (integer linear)
Overhead products from the demethanizer (C1a) go to the pressure swing absorber (PSA); bottom products go to the deethanizer (C3a). $Y^{C1a}_{a-b\|c-l} \Rightarrow Y^{\mathrm{PSA}}_{a\|b} \wedge Y^{C3a}_{c-e\|f-l}$ OR express the logical statement in the following way: From the demethanizer (C1a): • the overhead products go to the pressure swing absorber (PSA); • the bottom products go to the deethanizer (C3a).	$y^{\mathrm{PSA}}_{a\|b} - y^{\mathrm{C1a}}_{a\|b} \geq 0$ $y^{\mathrm{C3a}}_{c-e\|f-l} - y^{\mathrm{C1a}}_{a,\|b} \geq 0$
From the HP depropanizer (C1b): • the overhead products go to either the catalytic hydrogenation reactor (R1b) or extractive distillation column (C4b)	$y^{R1b}_{a-d,f-h\|e} + y^{C4b}_{a-d,f-h\|e} - y^{C1b}_{a-h\|f-l} \geq 0$ $y^{C8a}_{f-h\|j-l} - y^{C1b}_{a-h\|f-l} \geq 0$

- the bottom products go to the LP depropanizer (C8a).

$$Y^{C1b}_{a-h|f-l} \Rightarrow \left(Y^{R1b}_{a-d,f-h|e} \vee Y^{C4b}_{a-d,f-h|e}\right) \wedge Y^{C8a}_{f-h|j-l}$$

$$\left(\neg Y^{C1b}_{a-h|f-l} \vee Y^{R1b}_{a-d,f-h|e} \vee Y^{C4b}_{a-d,f-h|e}\right) \wedge \left(\neg Y^{C1b}_{a-h|f-l} \vee Y^{C8a}_{f-h|j-l}\right)$$

Overhead products from debutanizer (C1c) go to demethanizer (C2a), depropanizer (C2b) or debutanizer (C2c). Bottom products go to gasoline hydrogenation reactor (R4).

$$Y^{C1c}_{a-k|l} \Rightarrow \left(Y^{C2a}_{a-b|c-k} \vee Y^{C2b}_{a-h|f-k} \vee Y^{C2c}_{a-i|j-k}\right) \wedge Y^{R4}_{l}$$

$$\left(\neg Y^{C1c}_{a-k|l} \vee Y^{C2a}_{a-b|c-k} \vee Y^{C2b}_{a-h|f-k} \vee Y^{C2c}_{a-i|j-k}\right) \wedge \left(\neg Y^{C1c}_{a-k|l} \vee Y^{R4}_{l}\right)$$

$$y^{C2a}_{a-b|c-k} + y^{C2b}_{a-h|f-k} + y^{C2c}_{1-9|10,11} - y^{C2c}_{a-i|j-k} \geq 0$$

$$y^{R4}_{l} - y^{C1c}_{a-k|l} \geq 0$$

Overhead products from demethanizer (C2a) go to pressure swing absorber (PSA). Bottom products go to deethanizer(C3b) or debutanizer (C3c).

$$Y^{C2a}_{a-b|c-k} \Rightarrow Y^{PSA}_{a|b} \wedge \left(Y^{C3b}_{c-e|f-k} \vee Y^{C3c}_{c-e|j-k}\right)$$

$$\left(\neg Y^{C2a}_{a-b|c-k} \vee Y^{PSA}_{a|b}\right) \wedge \left(\neg Y^{C2a}_{a-b|c-k} \vee Y^{C3b}_{c-e|f-k} \vee Y^{C3c}_{c-e|j-k}\right)$$

$$y^{PSA}_{a|b} - y^{C2a}_{a-b|c-k} \geq 0$$

$$y^{C3b}_{c-e|f-k} + y^{C3c}_{c-e|j-k} - y^{C2a}_{a-b|c-k} \geq 0$$

Overhead products from depropanizer (C2b) go to catalytic hydrogenation reactor (R1b) or extractive distillation column (C4b). Bottom products go to depropanizer (C8b).

$$Y^{C2b}_{a-h|f-k} \Rightarrow \left(Y^{R1b}_{a-d,f-h|e} \vee Y^{C4b}_{a-d,f-h|e}\right) \wedge Y^{C8b}_{f-h|j-k}$$

$$\left(\neg Y^{C2b}_{a-h|f-k} \vee Y^{R1b}_{a-d,f-h|e} \vee Y^{C4b}_{a-d,f-h|e}\right) \wedge \left(\neg Y^{C2b}_{1-9|6-11} \vee Y^{C8b}_{f-h|j-k}\right)$$

$$y^{R1b}_{a-d,f-h|e} + y^{C4b}_{a-d,f-h|e} - y^{C2b}_{a-h|f-k} \geq 0$$

$$y^{C8b}_{f-h|j-k} - y^{C2b}_{a-h|f-k} \geq 0$$

Overhead products from depropanizer (C2c) go to catalytic hydrogenation reactor (R1b) or extractive distillation column (C4b). Bottom products go to extractive distillation column (C12)

$$Y^{C2c}_{a-h|j-k} \Rightarrow \left(Y^{R1b}_{a-d,f-h|e} \vee Y^{C4b}_{a-d,f-h|e}\right) \wedge \left(Y^{C12}_{j|k}\right)$$

$$\left(\neg Y^{C2c}_{a-h|j-k} \vee Y^{R1b}_{a-d,f-h|e} \vee Y^{C4b}_{a-d,f-h|e}\right) \wedge \left(\neg Y^{C2c}_{a-h|j-k} \vee Y^{C12}_{j|k}\right)$$

$$y^{R1b}_{a-d,f-h|e} + y^{C4b}_{a-d,f-h|e} - y^{C2c}_{a-h|j-k} \geq 0$$

$$y^{C12}_{j|k} - y^{C2c}_{a-h|j-k} \geq 0$$

Overhead products from the deethanizer (C3a) go to the catalytic hydrogenation reactor (R1a) or extractive distillation column (C4a). Bottom products go to depropanizer (C8a).

$$Y^{C3a}_{c-e|f-l} \Rightarrow \left(Y^{R1a}_{c-d|e} \vee Y^{C4a}_{c-d|e}\right) \wedge Y^{C8a}_{f-h|j-l}$$

$$\left(\neg Y^{C3a}_{c-e|f-l} \vee Y^{R1a}_{c-d|e} \vee Y^{C4a}_{c-d|e}\right) \wedge \left(\neg Y^{C3a}_{c-e|f-l} \vee Y^{C8a}_{f-h|j-l}\right)$$

$$y^{R1a}_{c-d|e} + y^{C4a}_{c-d|e} - y^{C3a}_{c-e|f-l} \geq 0$$

$$y^{C8a}_{f-h|j-l} - y^{C3a}_{c-e|f-l} \geq 0$$

Overhead products from the deethanizer (C3b) go to the catalytic hydrogenation reactor (R1a) or extractive distillation column (C4a). Bottom products go to depropanizer (C8b).

$$Y^{C3b}_{c-e|f-k} \Rightarrow \left(Y^{R1a}_{c-d|e} \vee Y^{C4a}_{c-d|e}\right) \wedge Y^{C8b}_{f-h|j-k}$$

$$\left(\neg Y^{C3b}_{c-e|f-k} \vee Y^{R1a}_{c-d|e} \vee Y^{C4a}_{c-d|e}\right) \wedge \left(\neg Y^{C3b}_{c-e|f-k} \vee Y^{C8b}_{f-h|j-k}\right)$$

$$y^{R1a}_{c-d|e} + y^{C4a}_{c-d|e} - y^{C3b}_{c-e|f-k} \geq 0$$

$$y^{C8b}_{f-h|j-k} - y^{C3b}_{c-e|f-k} \geq 0$$

Overhead products from debutanizer (C3c) go to catalytic hydrogenation reactor (R1c) or extractive distillation column (C4c). Bottom products go to extractive distillation column (C12) or C4 hydrogenatioan reactor (R3).

$$Y^{C3c}_{c-h|j-k} \Rightarrow \left(Y^{R1c}_{c-d,f-h|e} \vee Y^{C4c}_{c-d,f-h|e}\right) \wedge \left(Y^{C12}_{j|k} \vee Y^{R3}_{j|k}\right)$$

$$\left(\neg Y^{C3c}_{3-9|10,11} \vee Y^{R1c}_{c-d,f-h|e} \vee Y^{C4c}_{c-d,f-h|e}\right) \wedge \left(\neg Y^{C3c}_{3-9|10,11} \vee Y^{C12}_{j|k} \vee Y^{R3}_{j|k}\right)$$

$$y^{R1c}_{c-d,f-h|e} + y^{C4c}_{c-d,f-h|e} - y^{C3c}_{c-h|j-k} \geq 0$$

$$y^{C12}_{j|k} + y^{R3}_{j|k} - y^{C3c}_{c-h|j-k} \geq 0$$

Products from catalytic hydrogenation reactor (R1a) go to ethylene splitter (C10).

$$Y^{R1a}_{c-d|e} \Rightarrow Y^{C10}_{c|d}$$

$$\neg Y^{R1a}_{c-d|e} \vee Y^{C10}_{c|d}$$

$$y^{C10}_{c|d} - y^{R1a}_{c-d|e} \geq 0$$

Products from catalytic hydrogenation reactor (R1b) go to demethanizer (C5a) or depropanizer (C5c).

$$Y^{R1b}_{a-d,f-h|e} \Rightarrow Y^{C5a}_{a-b|c-d,f-h} \vee Y^{C5c}_{a-d|f-h}$$

$$\neg Y^{R1b}_{a-d,f-h|5} \vee Y^{C5a}_{a-b|c-d,f-h} \vee Y^{C5c}_{a-d|f-h}$$

$$y^{C5a}_{a-b|c-d,f-h} + y^{C5c}_{a-d|f-h} - y^{R1b}_{a-d,f-h|e} \geq 0$$

Products from catalytic hydrogenation reactor (R1c) go to demethanizer (C5b).

$$Y^{R1c}_{c-d,f-h|e} \Rightarrow Y^{C5b}_{c-d|f-h}$$

$$\neg Y^{R1c}_{c-d,f-h|e} \vee Y^{C5b}_{c-d|f-h}$$

$$y^{C5b}_{c-d|f-h} - y^{R1c}_{c-d,f-h|e} \geq 0$$

Overhead products of extractive distillation (C4a) go to ethylene splitter (C10).

$$Y^{C4a}_{c-d|e} \Rightarrow Y^{C10}_{c|d}$$

$$\neg Y^{C4a}_{c-d|e} \vee Y^{C10}_{c|d}$$

$$y^{C10}_{c|d} - y^{C4a}_{c-d|e} \geq 0$$

Overhead products from extractive distillation (C4b) go to demethanizer (C5a) or depropanizer (C5c).

$$y^{C5a}_{a-b|c-d,f-h} + y^{C5c}_{a-d|f-h} - y^{C4b}_{a-d,f-h|e} \geq 0$$

$$Y^{C4b}_{a-d,f-h|e} \Rightarrow Y^{C5a}_{a-b|c-d,f-h} \vee Y^{C5c}_{a-d|f-h}$$
$$\neg Y^{C4b}_{a-d,f-h|e} \vee \left(Y^{C5a}_{a-b|c-d,f-h} \vee Y^{C5c}_{a-d|f-h} \right)$$

(NOTE: Boolean variable for column C5b $Y^{C5b}_{3,4|6-9}$ is not considered in the logic proposition because it does not involve components 1 and 2.)

Overhead products from extractive distillation (C4c) go to deeethanizer (C5b)

$$Y^{C4c}_{c-d,f-h|e} \Rightarrow Y^{C5b}_{c-d|f-h}$$
$$\neg Y^{C4c}_{c-d,f-h|e} \vee Y^{C5b}_{c-d|f-h}$$

$$y^{C5b}_{c-d|f-h} - y^{C4c}_{c-d,f-h|e} \geq 0$$

Overhead products demethanizer (C5a) go to pressure swing absorber (PSA). Bottom products go to deethanizer (C7).

$$Y^{C5a}_{a-b|c-d,f-h} \Rightarrow Y^{PSA}_{a|b} \wedge Y^{C7}_{c-d|f-h}$$
$$\left(\neg Y^{C5a}_{a-b|c-d,f-h} \vee Y^{PSA}_{a|b} \right) \wedge \left(\neg Y^{C5a}_{a-b|c-d,f-h} \vee Y^{C7}_{c-d|f-h} \right)$$

$$y^{PSA}_{a|b} - y^{C5a}_{a-b|c-d,f-h} \geq 0$$
$$y^{C7}_{c-d|f-h} - y^{C5a}_{a-b|c-d,f-h} \geq 0$$

Overhead products demethanizer (C5b) go to ethylene splitter (C10). Bottom products go to methyl acetylene & propadiene reactor (R2).

$$Y^{C5b}_{c-d|f-h} \Rightarrow Y^{C10}_{c|d} \wedge Y^{R2}_{f-h}$$
$$\left(\neg Y^{C5b}_{c-d|f-h} \vee Y^{C10}_{c|d} \right) \wedge \left(\neg Y^{C5b}_{c-d|f-h} \vee Y^{R2}_{f-h} \right)$$

$$y^{C10}_{c|d} - y^{C5b}_{c-d|f-h} \geq 0$$
$$y^{R2}_{f-h} - y^{C5b}_{3,4|6-9} \geq 0$$

Overhead products depropanizer (C5c) go to demethanizer (C6). Bottom products go to methyl acetylene & propadiene reactor (R2).

$$Y^{C5c}_{a-d|c-d,f-h} \Rightarrow Y^{C6}_{a-b|c-d} \wedge Y^{R2}_{f-h}$$
$$\left(\neg Y^{C5c}_{a-d|c-d,f-h} \vee Y^{C6}_{a-b|c-d} \right) \wedge \left(\neg Y^{C5c}_{a-d|c-d,f-h} \vee Y^{R2}_{f-h} \right)$$

$$y^{C6}_{a-b|c-d} - y^{C5c}_{a-d|c-d,f-h} \geq 0$$
$$y^{R2}_{f-h} - y^{C5c}_{a-d|c-d,f-h} \geq 0$$

Overhead products of demethanizer (C6) go to pressure swing absorber (PSA) and the bottom product go to ethylene splitter (C10).

$$Y^{C6}_{a-b|c-d} \Rightarrow Y^{PSA}_{a|b} \wedge Y^{C10}_{c|d}$$
$$\left(\neg Y^{C6}_{a-b|c-d} \vee Y^{PSA}_{a|b} \right) \wedge \left(\neg Y^{C6}_{a-b|c-d} \vee Y^{C10}_{c|d} \right)$$

$$y^{PSA}_{a|b} - y^{C6}_{a-b|c-d} \geq 0$$
$$y^{C10}_{c|d} - y^{C6}_{a-b|c-d} \geq 0$$

Overhead product from deethanizer (C7) go to ethylene splitter (C10) and bottom product go to methyl acetylene & propadiene reactor (R2). $Y_{c-d\mid f-h}^{C7} \Rightarrow Y_{c\mid d}^{C10} \wedge Y_{f-h}^{R2}$ $\left(\neg Y_{c-d\mid f-h}^{C7} \vee Y_{c\mid d}^{C10}\right) \wedge \left(\neg Y_{c-d\mid f-h}^{C7} \vee Y_{f-h}^{R2}\right)$	$y_{c\mid d}^{C10} - y_{c-d\mid f-h}^{C7} \geq 0$ $y_{f-h}^{R2} - y_{c-d\mid f-h}^{C7} \geq 0$
Overhead products from depropanizer (C8a) go to methyl acetylene & propadiene reactor (R2). Bottom products will either got to debutanizer (C9) or olefin cracking unit (OCU). $Y_{f-h\mid j-l}^{C8a} \Rightarrow Y_{f-h}^{R2} \wedge \left(Y_{j-k\mid l}^{C9} \vee Y_{j-l}^{OCU}\right)$ $\left(\neg Y_{6-9\mid 10-12,14-18}^{C8a} \vee Y_{f-h}^{R2}\right) \wedge \left(\neg Y_{f-h\mid j-l}^{C8a} \vee Y_{j-k\mid l}^{C9} \vee Y_{j-l}^{OCU}\right)$	$y_{f-h}^{R2} - y_{f-h\mid j-l}^{C8a} \geq 0$ $y_{j-k\mid l}^{C9} + y_{j-l}^{OCU} - y_{f-h\mid j-l}^{C8a} \geq 0$
Overhead products from depropanizer (C8b) go to methyl acetylene and propadiene reactor (R2). Bottom products will either go to C4 hydrogenation reactor (R3), extractive distillation (C12) $Y_{f-h\mid j-k}^{C8b} \Rightarrow Y_{f-h}^{R2} \wedge \left(Y_{j\mid k}^{R3} \vee Y_{j\mid k}^{C12}\right)$ $\left(\neg Y_{f-h\mid j-k}^{C8b} \vee Y_{f-h}^{R2}\right) \wedge \left(\neg Y_{6-9\mid 10-11}^{C8b} \vee Y_{j\mid k}^{R3} \vee Y_{j\mid k}^{C12}\right)$	$y_{f-h}^{R2} - y_{f-h\mid j-k}^{C8b} \geq 0$ $y_{j\mid k}^{R3} + y_{j\mid k}^{C12} - y_{f-h\mid j-k}^{C8b} \geq 0$
Products from methyl acetylene and propadiene reactor (R2) go to propylene splitter (C11) (*note*: equivalence relation is used in the logical statement because involving single choice decision) $Y_{f-h}^{R2} \Leftrightarrow Y_{f\mid g}^{C11}$ $\left(\neg Y_{f-h}^{R2} \vee Y_{f\mid g}^{C11}\right) \wedge \left(Y_{f-h}^{R2} \vee \neg Y_{f\mid g}^{C11}\right)$	$y_{f\mid g}^{C11} - y_{f-h}^{R2} \geq 0$ $y_{f-h}^{R2} - y_{f\mid g}^{C11} \geq 0$
Overhead products from debutanizer (C9) will either go to C4 hydrogenation reactor (R3) or extractive distillation (C12). Bottom products go to gasoline hydrogenation reactor (R4). $Y_{j-k\mid l}^{C9} \Rightarrow \left(Y_{j\mid k}^{R3} \vee Y_{j\mid k}^{C12}\right) \wedge Y_{l}^{R4}$ $\left(\neg Y_{j-k\mid l}^{C9} \vee Y_{j\mid k}^{R3} \vee Y_{j\mid k}^{C12}\right) \wedge \left(\neg Y_{j-k\mid l}^{C9} \vee Y_{l}^{R4}\right)$	$y_{j\mid k}^{R3} + y_{j\mid k}^{C12} - y_{j-k\mid l}^{C9} \geq 0$ $y_{l}^{R4} - y_{j-k\mid l}^{C9} \geq 0$

Table ~~7~~8(b) Logical constraints on structural specifications that involve inlet/feed to columns

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).	$y^{C3c}_{c-h\|j-k} - y^{R1c}_{c-d,f-h\|e} \geq 0$

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$$Y^{R1c}_{c-d,f-h|e} \Rightarrow Y^{C3c}_{c-h|j-k}$$

$$\neg Y^{R1c}_{c-d,f-h|e} \vee Y^{C3c}_{c-h|j-k}$$

The inlet of extractive distillation (C4a) is either from deethanizer (C3a) or deethanizer (C3b).

$$y^{C3a}_{c-e|f-l} + y^{C3b}_{c-e|f-k} - y^{C4a}_{c-d|e} \geq 0$$

$$Y^{C4a}_{c-d|e} \Rightarrow Y^{C3a}_{c-e|f-l} \vee Y^{C3b}_{c-e|f-k}$$

$$\neg Y^{C4a}_{c-d|e} \vee Y^{C3a}_{c-e|f-l} \vee Y^{C3b}_{c-e|f-k}$$

The inlet of extractive distillation (C4b) is either from depropanizer (C2b), debutanizer (C2c) or HP depropanizer (C1b).

$$y^{C2b}_{a-h|f-k} + y^{C2c}_{a-h|j-k} + y^{C1b}_{a-k|l} - y^{C4b}_{a-d,f-h|e} \geq 0$$

$$Y^{C4b}_{a-d,f-h|e} \Rightarrow Y^{C2b}_{a-h|f-k} \vee Y^{C2c}_{a-h|j-k} \vee Y^{C1b}_{a-k|l}$$

$$\neg Y^{C4b}_{a-d,f-h|e} \vee Y^{C2b}_{a-h|f-k} \vee Y^{C2c}_{a-h|j-k} \vee Y^{C1b}_{a-k|l}$$

The inlet of extractive distillation (C4c) is from debutanizer (C3c).

$$y^{C3c}_{c-h|j-k} - y^{C4c}_{c-d,f-h|e} \geq 0$$

$$Y^{C4c}_{c-d,f-h|e} \Rightarrow Y^{C3c}_{c-h|j-k}$$

$$\neg Y^{C4c}_{c-d,f-h|e} \vee Y^{C3c}_{c-h|j-k}$$

The inlet of demethanizer (C5a) or depropanizer (C5c) is either from catalytic hydrogenation reactor (R1b) or extractive distillation (C4b).

$$y^{R1b}_{a-d,f-h|e} + y^{C4b}_{a-d,f-h|e} - y^{C5a}_{a-b|c-d,f-h} \geq 0$$

$$y^{R1b}_{a-d,f-h|e} + y^{C4b}_{a-d,f-h|e} - y^{C5c}_{a-d|f-h} \geq 0$$

$$Y^{C5a}_{a-b|c-d,f-h} \vee Y^{C5c}_{a-d|f-h} \Rightarrow Y^{R1b}_{a-d,f-h|e} \vee Y^{C4b}_{a-d,f-h|e}$$

$$(\neg Y^{C5a}_{a-b|c-d,f-h} \wedge \neg Y^{C5c}_{a-d|f-h}) \vee (Y^{R1b}_{1-4,6-9|5} \vee Y^{C4b}_{1-4,6-9|5})$$

The inlet of deethanizer (C5b) is either from catalytic hydrogenation reactor (R1c) or extractive distillation (C4c).

$$y^{R1c}_{c-d,f-h|e} + y^{C4c}_{c-d,f-h|e} - y^{C5b}_{c-d|f-h} \geq 0$$

$$Y^{C5b}_{c-d|f-h} \Rightarrow Y^{R1c}_{c-d,f-h|e} \vee Y^{C4c}_{c-d,f-h|e}$$

$$\neg Y^{C5b}_{c-d|f-h} \vee Y^{R1c}_{c-d,f-h|e} \vee Y^{C4c}_{c-d,f-h|e}$$

The inlet of demethanizer (C6) is from depropanizer (C5c).

$$y^{C5c}_{a-d|f-h} - y^{C6}_{a-b|c-d} \geq 0$$

$$Y^{C6}_{a-b|c-d} \Rightarrow Y^{C5c}_{a-d|f-h}$$

$$\neg Y^{C6}_{a-b|c-d} \vee Y^{C5c}_{a-d|f-h}$$

The inlet of deethanizer (C7) is from demethanizer (C5a).

$$y^{C5a}_{a-b|c-d,f-h} - y^{C7}_{c-d|f-h} \geq 0$$

$$Y_{c-d|f-h}^{C7} \Rightarrow Y_{a-b|c-d,f-h}^{C5a}$$

$$\neg Y_{c-d|f-h}^{C7} \vee Y_{a-b|c-d,f-h}^{C5a}$$

The inlet to depropanizer (C8a) is either from deethanizer (C3a) or HP depropanizer (C1b).

$$y_{c-e|f-l}^{C3a} + y_{a-h|f-l}^{C1b} - y_{f-h|j-l}^{C8a} \geq 0$$

$$Y_{f-h|j-l}^{C8a} \Rightarrow Y_{c-e|f-l}^{C3a} \vee Y_{a-h|f-l}^{C1b}$$

$$\neg Y_{f-h|j-l}^{C8a} \vee Y_{c-e|f-l}^{C3a} \vee Y_{a-h|f-l}^{C1b}$$

The inlet to depropanizer (C8b) is either from deethanizer (C3b) or HP depropanizer (C2b).

$$y_{c-e|f-k}^{C3b} + y_{a-h|f-k}^{C2b} - y_{f-h|j-k}^{C8b} \geq 0$$

$$Y_{f-h|j-k}^{C8b} \Rightarrow Y_{c-e|f-k}^{C3b} \vee Y_{a-h|f-k}^{C2b}$$

$$\neg Y_{f-h|j-k}^{C8b} \vee Y_{c-e|f-k}^{C3b} \vee Y_{a-h|f-k}^{C2b}$$

The inlet of olefin cracking unit (OCU) is either from depropanizer (C8a) or depropanizer (C8b).

$$y_{f-h|j-l}^{C8a} + y_{f-h|j-k}^{C8b} - y_{j-l}^{OCU} \geq 0$$

$$Y_{j-l}^{OCU} \Rightarrow Y_{f-h|j-l}^{C8a} \vee Y_{f-h|j-k}^{C8b}$$

$$\neg Y_{j-l}^{OCU} \vee Y_{f-h|j-l}^{C8a} \vee Y_{f-h|j-k}^{C8b}$$

The inlet of MAPD(R2) is from either from C7, C5b, C5c, C8a or C8b.

$$y_{c-d|f-h}^{C7} + y_{c-d|f-h}^{C5b} + y_{a-d|f-h}^{C5c} + y_{f-h|j-l}^{C8a} + y_{f-h|j-k}^{C8b} - y_{f-h}^{R2} \geq 0$$

$$Y_{f-h}^{R2} \Rightarrow Y_{c-d|f-h}^{C7} \vee Y_{c-d|f-h}^{C5b} \vee Y_{a-d|f-h}^{C5c} \vee Y_{f-h|j-l}^{C8a} \vee Y_{f-h|j-k}^{C8b}$$

$$\neg Y_{f-h}^{R2} \vee Y_{c-d|f-h}^{C7} \vee Y_{c-d|f-h}^{C5b} \vee Y_{a-d|f-h}^{C5c} \vee Y_{f-h|j-l}^{C8a} \vee Y_{f-h|j-k}^{C8b}$$

The inlet to pressure swing absorber (PSA) is either from demethanizer (C1a), demethanizer (C2a), demethanizer (C5a) or demethanizer (C6).

$$y_{a-b|c-l}^{C1a} + y_{a-b|c-k}^{C2a} + y_{a-b|c-d,f-h}^{C5a} + y_{a-b|c-d}^{C6} - y_{a|b}^{PSA} \geq 0$$

$$Y_{a|b}^{PSA} \Rightarrow Y_{a-b|c-l}^{C1a} \vee Y_{a-b|c-k}^{C2a} \vee Y_{a-b|c-d,f-h}^{C5a} \vee Y_{a-b|c-d}^{C6}$$

$$\neg Y_{a|b}^{PSA} \vee Y_{a-b|c-l}^{C1a} \vee Y_{a-b|c-k}^{C2a} \vee Y_{a-b|c-d,f-h}^{C5a} \vee Y_{a-b|c-d}^{C6}$$

The inlet of debutanizer (C9) is from depropanizer (C8a).

$$y_{f-h|j-l}^{C8a} - y_{j-k|l}^{C9} \geq 0$$

$$Y_{j-k|l}^{C9} \Rightarrow Y_{f-h|j-l}^{C8a}$$

$$\neg Y_{j-k|l}^{C9} \vee Y_{f-h|j-l}^{C8a}$$

The inlet to ethylene splitter (C10) is either from catalytic hydrogenation reator (R1a), extractive distillation (C4a), depropanizer (C5) or demethanizer (C6) or deethanizer (C7).

$$y_{c-d|e}^{R1a} + y_{c-d|e}^{C4a} + y_{c-d|f-h}^{C5b} + y_{a-b|c-d}^{C6} + y_{c-d|f-h}^{C7} - y_{c|d}^{C10} \geq 0$$

$Y_{c\|d}^{C10} \Rightarrow Y_{c-d\|e}^{R1a} \vee Y_{c-d\|e}^{C4a} \vee Y_{c-d\|f-h}^{C5b} \vee Y_{a-b\|c-d}^{C6} \vee Y_{c-d\|f-h}^{C7}$ $\neg Y_{c\|d}^{C10} \vee Y_{c-d\|e}^{R1a} \vee Y_{c-d\|e}^{C4a} \vee Y_{c-d\|f-h}^{C5b} \vee Y_{a-b\|c-d}^{C6} \vee Y_{c-d\|f-h}^{C7}$	
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). $Y_{l}^{R4} \Rightarrow Y_{j-k\|l}^{C9} \vee Y_{a-k\|l}^{C1c}$ $\neg Y_{l}^{R4} \vee Y_{j-k\|l}^{C9} \vee Y_{a-k\|l}^{C1c}$	$y_{j-k\|l}^{C9} + y_{a-k\|l}^{C1c} - y_{l}^{R4} \geq 0$

4.4 Switching Constraints

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

$$F_k \le M_k y_k \qquad (7)$$

where F_k = total flowrate of an input stream for process unit k in kg/day,

M_k = maximum capacity of process unit k

y_k = existence or non existence of process unit k.

We could see that when $y_i = 0$ (unit does not exist), then the constraint (7) becomes:

$$F_k \le 0 \qquad (8)$$

but flowrate variables are either zero or takes on positive values, so equation (8) becomes $F_k = 0$, which stipulates the condition of zero input flowrate into a non-existing unit. When $y_k = 1$ (unit exists), then the constraint (7) becomes:

$$F_k \le M_k \qquad (9)$$

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.

For example equation (7), if the maximum capacity of a distillation column is equals to 100 m^3, then the big-M logical constraint for that unit becomes

$$F_k \le \left(100 \text{ m}^3\right) y_k \qquad (8)$$

This constraint (7) is usually written for the input flowrate because it can be related to the output flowrates through the material balances.

The big-*M* logical constraints are also sometimes termed as switching constraints in the literature (Rardin, 1998, p. 558). 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 $_i \leq M_i z_i$ 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, *ta*ken to be an arbitrarily large number, 1000, which it acts as an upper bound for the corresponding feed flow rate of the initial mixture.

Table 9~~98~~ Switching constraints for the separation subsystem using intermediate representation

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Task/Process Unit	Switching Constraint
C1	$F^{C1a} \leq M_{C1a} y^{C1a}$ $F^{C1b} \leq M_{C1b} y^{C1b}$ $F^{C1c} \leq M_{C1c} y^{C1c}$
C2	$F^{C2a} \leq M_{C2a} y^{C2a}$ $F^{C2b} \leq M_{C2b} y^{C2b}$ $F^{C2c} \leq M_{C2c} y^{C2c}$
C3	$F^{C3a} \leq M_{C3a} y^{C3a}$ $F^{C3b} \leq M_{C3b} y^{C3b}$ $F^{C3c} \leq M_{C3c} y^{C3c}$
R1	$F^{R1a} \leq M_{R1a} y^{R1a}$ $F^{R1b} \leq M_{R1b} y^{R1b}$ $F^{R1c} \leq M_{R1b} y^{R1c}$
C4	$F^{C4a} \leq M_{C4a} y^{C4a}$ $F^{C4b} \leq M_{C4b} y^{C4b}$ $F^{C4c} \leq M_{C4c} y^{C4c}$

C5	$F^{\mathrm{C5}a} \le M_{\mathrm{C5}a} y^{\mathrm{C5}a}$ $F^{\mathrm{C5}b} \le M_{\mathrm{C5}b} y^{\mathrm{C5}b}$ $F^{\mathrm{C5}c} \le M_{\mathrm{C5}c} y^{\mathrm{C5}c}$
C6	$F^{\mathrm{C6}} \le M_{\mathrm{C6}} y^{\mathrm{C6}}$
C7	$F^{\mathrm{C7}} \le M_{\mathrm{C7}} y^{\mathrm{C7}}$
C8	$F^{\mathrm{C8}a} \le M_{\mathrm{C8}a} y^{\mathrm{C8}a}$ $F^{\mathrm{C8}b} \le M_{\mathrm{C8}b} y^{\mathrm{C8}b}$
R2	$F^{\mathrm{R2}} \le M_{\mathrm{R2}} y^{\mathrm{R2}}$
C9	$F^{\mathrm{C9}} \le M_{\mathrm{C9}} y^{\mathrm{C9}}$
C10	$F^{\mathrm{C10}} \le M_{\mathrm{C10}} y^{\mathrm{C10}}$
C11	$F^{R2}_{8,9\rightarrow 6,7} \le M_{\mathrm{C11}} y^{\mathrm{C11}}_{6\|7}$
R3	$F^{\mathrm{R3}} \le M_{\mathrm{R3}} y^{\mathrm{R3}}$
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	$F^{R4} \le M_{\mathrm{R4}} y^{R4}$

The complete formulation of the optimization model for the distillation sequences for olefin production is summarized as follows~~presented as below~~:

$$
\begin{aligned}
&\min \quad Z = \sum_{k\in COL} \mathrm{CAPEX}_k y_k + \sum_{k\in COL} \mathrm{OPEX}_k F_k \\
&\text{s.t} \\
&\quad \sum_{k\in FS_F} F_k = F_{TOT} \\
&\quad \sum_{k\in PS_m} \xi_k F_k - \sum_{k\in FS_m} F_k = 0 \quad m \in IP \quad (\text{material balances for each intermediate product}) \\
&\quad F_k \le M_k y_k \qquad \forall k \in COL \qquad (\text{big-}M \text{ logical constraints}) \\
&\quad \sum_{k\in FS_F} y_k = 1 \qquad (\text{logical constraints on leading columns}) \\
&\quad \sum_{k\in m} y_k \le 1 \qquad (\text{logical constraints on intermediate columns}) \\
&\quad \sum_{k\in PS_m} y_k - \sum_{k\in FS_m} y_k \ge 0 \qquad (\text{logical constraints on structural specifications}) \\
&\quad y_k = 0 \text{ or } 1 \qquad \forall k \in COL
\end{aligned}
$$

The decision variables in this formulation are the binary variable, y_k and the flowrates to each column, F_k.

CHAPTER 5

COMPUTATIONAL EXPERIMENTS AND DISCUSSIONS ON NUMERICAL RESULTS

To demonstrate the implementation of the proposed model formulation for determining the optimal separation sequence, we consider different olefin feedstock as the feed composition~~s~~ and by utilizing the method of integer cuts constraints.

5.1 Comparison of distillation sequencing using different olefin feedstocks

Three cases of different olefin feedstock are evaluated using our proposed model formulation.

5.1.1 Case 1: Ethane feedstock from Ethylene Polyethylene (M) Sdn. Bhd (EPEMSB)

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Table 10~~109~~ Typical yields of ethane feedstock from EPEMSB

	Feed Composition of Ethane Yield	
No:	**Group of Compounds**	**Typical Yields (wt %)**
a	Methane , CH_4	24.56
b	Hydrogen ,H_2	0.65
c	Ethane, C_2H_6	27.91
d	Ethylene , C_2H_4	41.83
e	Acetylene , C_2H_2	0.32
f	Propane , C_3H_8	0.22
g	Propylene, C_3H_6	1.12
h	Propadiene/ Methylacetyl , C_3H_4	0.02
j	Butadiene, 1,3-C_4H_6	1.23
k	C4s , Butene & Butane	0.35
l	Pyrolysis Gasoline	1.67
m	Fuel Oil	0.12

This feed composition of ethane yield from EPEMSB as shown in Table ~~9~~ 10 is tested in our optimization model. The optimum distillation sequence from the result is shown in Figure ~~12~~11.

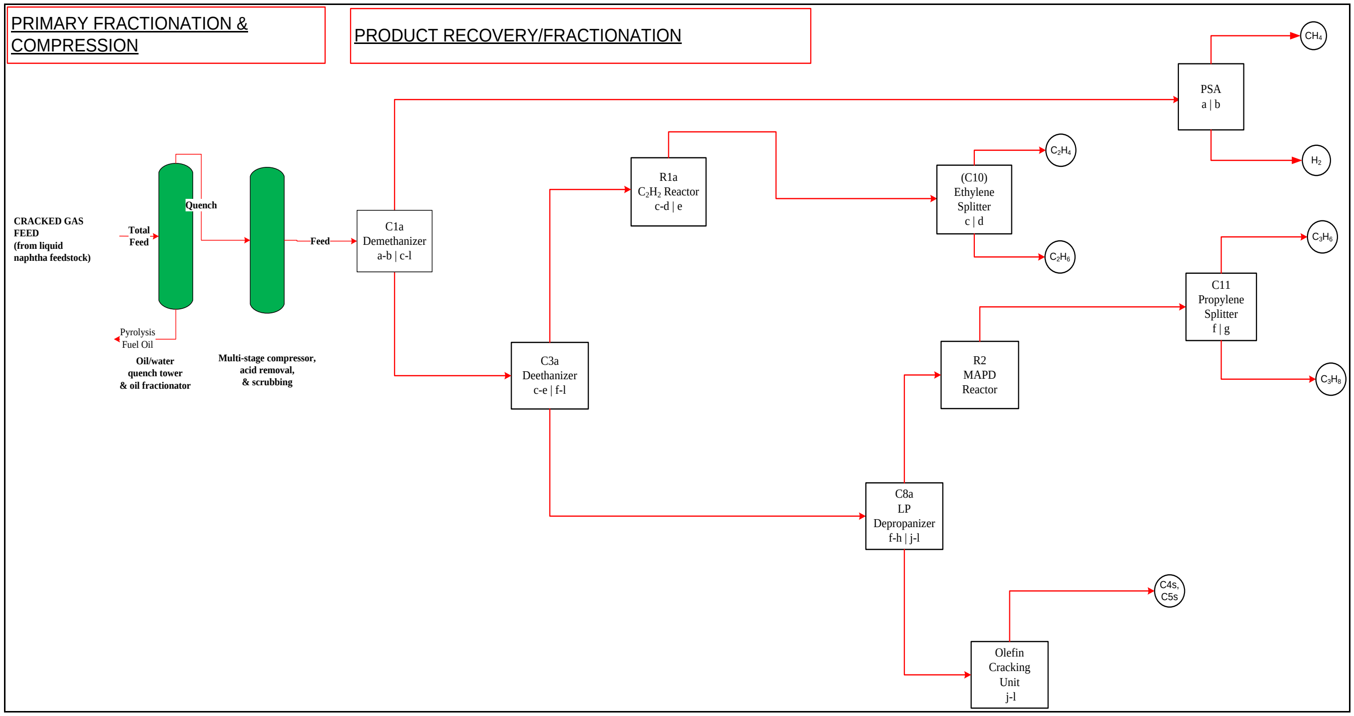

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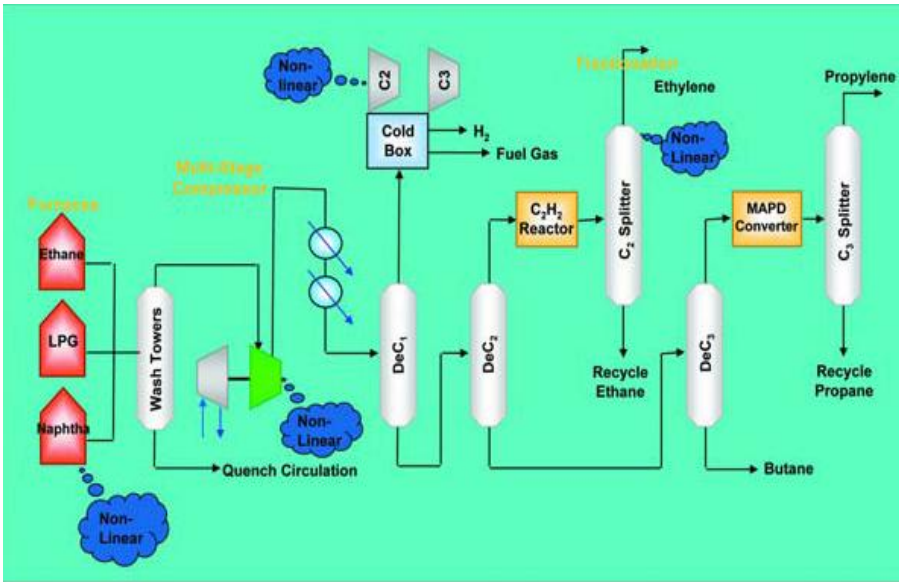
Figure ~~12~~ 6 Optimal flowsheet distillation sequence for Ethane Feedstock from EPEMSB



~~**Figure 13 Flowsheet configuration for Ethylene Polyethylene (M) Sdn. Bhd., which uses ethane as the feedstock**~~

~~Compared to the distillation column sequence of the existing configuration of the ethylene plant of Ethylene Polyethylene (M) Sdn. Bhd (Figure 13)., which uses ethane as its feedstock, the optimal distillation sequence obtained from our computational experiments differs only in that the Pressure Swing Absorption (PSA) is also selected.~~

The optimal solution is in agreement with the following three common heuristic guidelines for distillation sequencing in accordance with Douglas et al. (1985):

Heuristic 1. Remove the lightest component first and;

~~Heuristic 2. Remove the most plentiful component first; and~~

Heuristic 3: perform difficult separation last.

The optimal solution follows h~~H~~euristic 1 as the first column is the demethanizer, which removes the lightest components of hydrogen and methane first. This is known as the direct sequence, which requires less energy as the light material (hydrogen and methane) is vaporized once in the direct sequence. In another way, it requires less minimum vapor flow rate for reboiler duty and condenser duty.

~~The optimal solution also follows the Hheuristic 2 as the bottom of demethanizer goes to deethanizer in order to remove the most plentiful components first, which is C2s at the top and C3s above at the bottom of the task Depropanizer (C3a).~~ Besides that, the optimal solution also performs the difficult separation last which is consistent with ~~the~~ ~~H~~heuristic 3~~.~~,e.g. propylene fractionator and ethylene fractionator.

5.1.2 Case 2: Naphtha Composition from University of Manchester's Centre for Process Integration (CPI) (2005)

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Table 11~~11~~~~10~~ Typical yields of naphtha feedstock taken from ~~University of Manchester's Centre for Process Integration~~ CPI (2005)

Feed Composition of Naphtha Cracking Yield from UMIST		
No:	**Group of Compounds**	**Typical Yields (wt %)**
a	Methane , CH4	15.3
b	Hydrogen ,H2	0.8
c	Ethane, C2H6	3.8
d	Ethylene , C2H4	29.3
e	Acetylene , C2H2	0.7
f	Propane , C3H8	0.3
g	Propylene, C3H6	14.1
h	Propadiene , C3H4	1.1
j	Butadiene, 1,3-C4H6	4.8
k	C4s , Butene & Butane	4.5
l	Pyrolysis Gasoline	21
m	Fuel Oil	3.8

The~~is~~ feed composition of typical naphtha ~~typical~~ yield as reported by ~~from~~ University of Manchester's Centre for Process Integration or ~~University of Manchester's Centre for Process Integration~~CPI, for short, ~~(2005)~~ is~~which~~ shown in Table ~~10~~ 11 and~~is~~ tested in our optimization model. The optimum distillation sequencing using this naphtha feedstock ~~from University of Manchester's Centre for Process Integration (2005)~~ produces ~~from~~ the optimal flowsheet~~result~~ ~~is~~ shown in Figure ~~14~~12.

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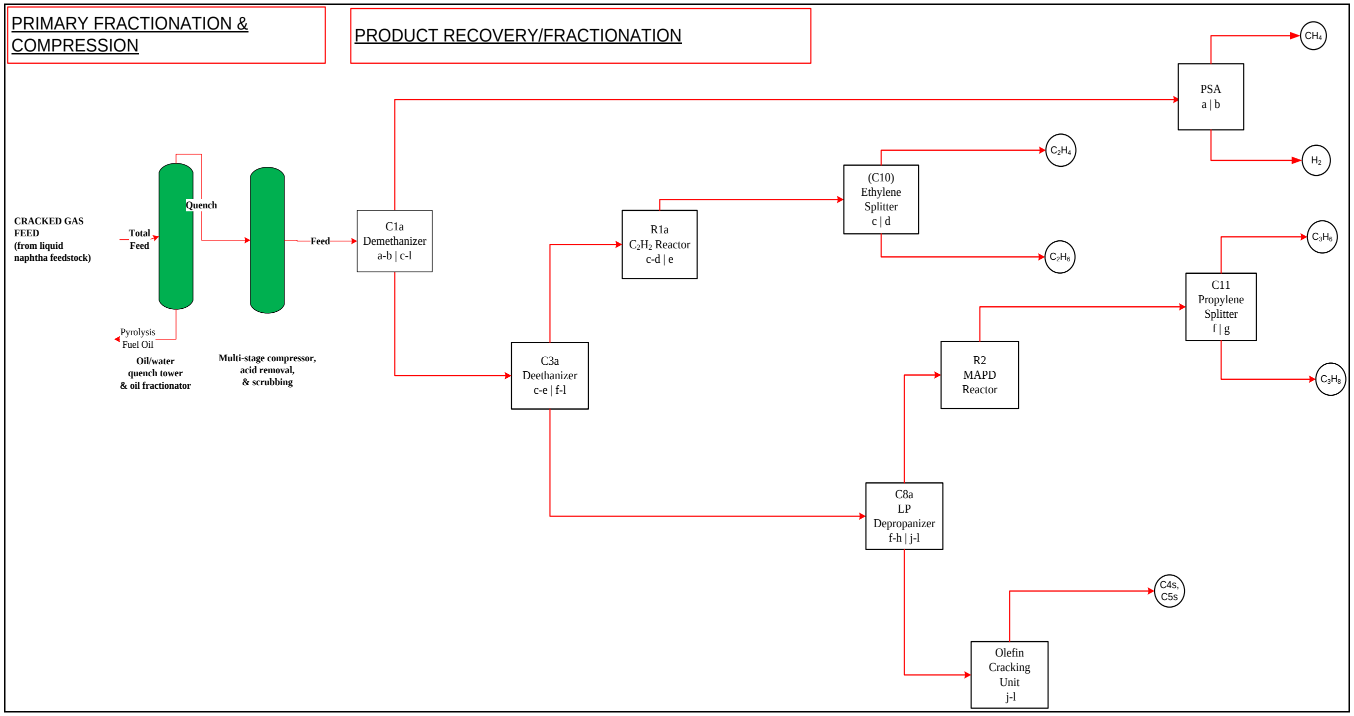

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~~Figure 14~~

Figure 7–Optimal flowsheet for distillation sequencing using naphtha composition from University of Manchester's Centre for Process Integration (2005)

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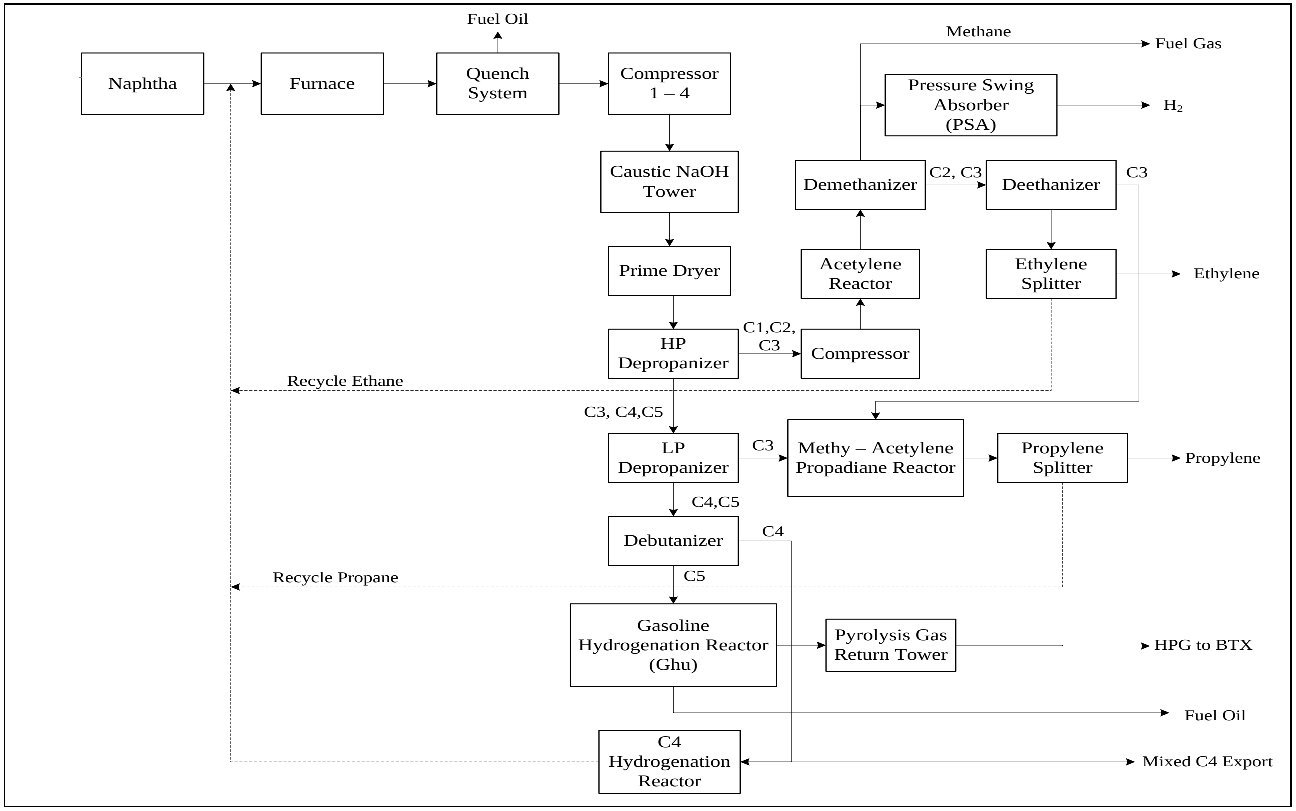
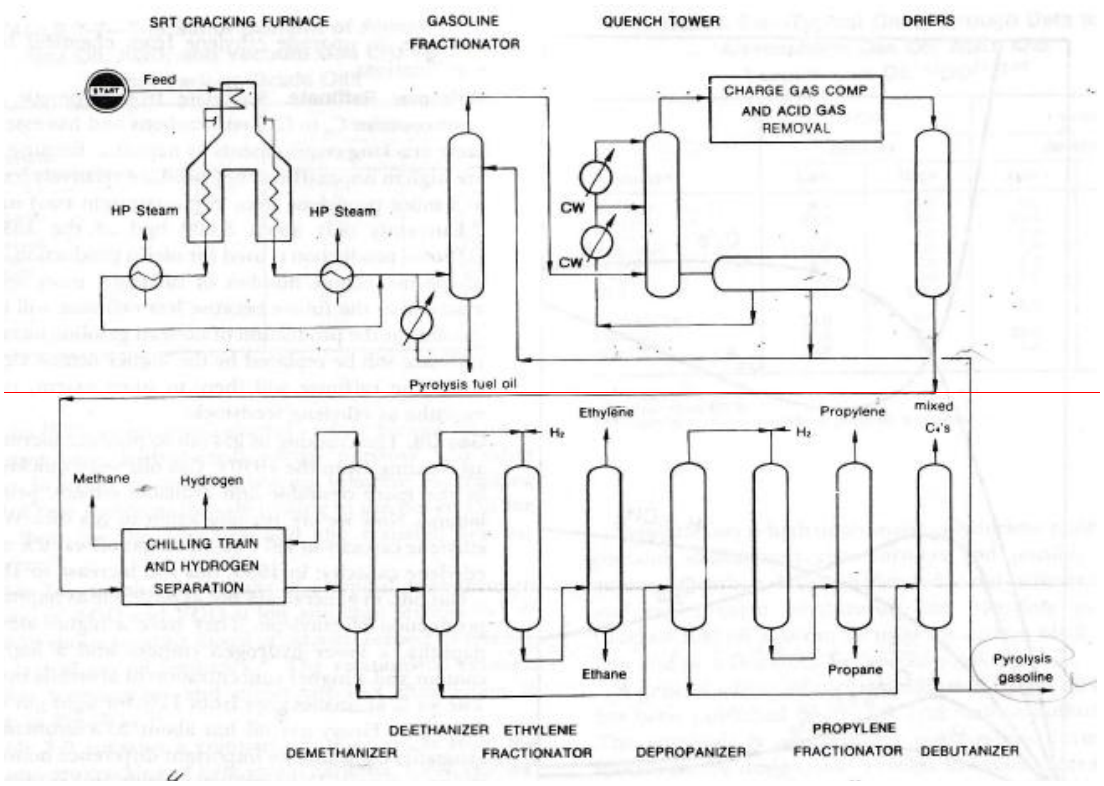


Figure ~~15~~ 8 Flowsheet Configuration from Titan Petrochemicals (M) Sdn. Bhd


SRT CRACKING FURNACE
GASOLINE FRACTIONATOR
QUENCH TOWER
DRIERS
START
Feed
CHARGE GAS COMP AND ACID GAS REMOVAL
HP Steam
HP Steam
CW
CW
Pyrolysis fuel oil
Ethylene
H_2
Propylene
mixed C_4's
H_2
Methane
Hydrogen
CHILLING TRAIN AND HYDROGEN SEPARATION
Ethane
Propane
Pyrolysis gasoline
DEETHANIZER
ETHYLENE FRACTIONATOR
DEMETHANIZER
DEPROPANIZER
PROPYLENE FRACTIONATOR
DEBUTANIZER

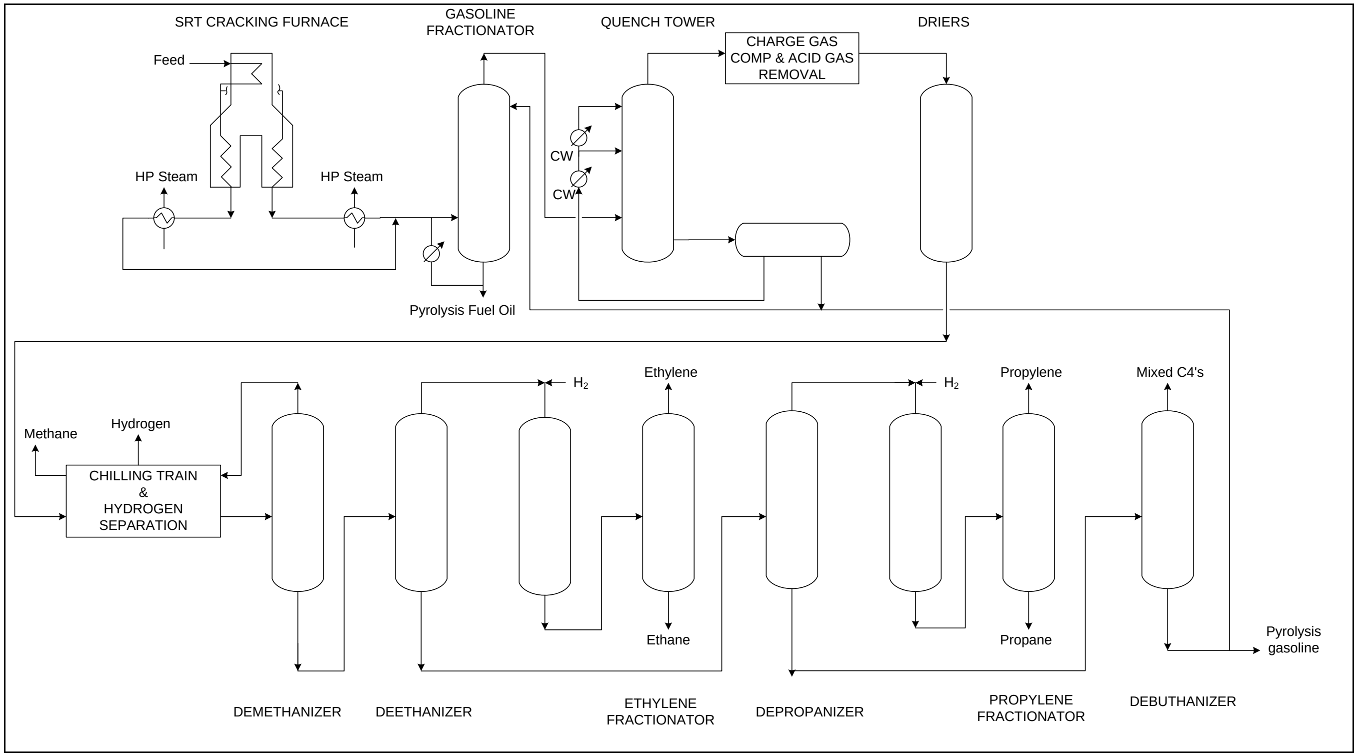

SRT CRACKING FURNACE
GASOLINE FRACTIONATOR
QUENCH TOWER
CHARGE GAS COMP & ACID GAS REMOVAL
DRIERS
Feed
HP Steam
HP Steam
CW
CW
Pyrolysis Fuel Oil
Methane
Hydrogen
CHILLING TRAIN & HYDROGEN SEPARATION
H_2
Ethylene
H_2
Propylene
Mixed C4's
Ethane
Propane
Pyrolysis gasoline
DEMETHANIZER
DEETHANIZER
ETHYLENE FRACTIONATOR
DEPROPANIZER
PROPYLENE FRACTIONATOR
DEBUTHANIZER

Figure ~~16~~ 9 The C-E Lummus process for the cracking of naphtha or gas oil for the production of ethylene (H~~ydrocarbon Processing~~atch & Matar, 1975)

~~The optimal distillation sequence obtained from our computational experiments using naphtha composition from University of Manchester's Process Integration (2005) is different from Titan Petrochemical (M) Sdn. Bhd. However, the optimal distillation sequence obtained from our model formulation using naphtha composition from University of Manchester's Process Integration (2005) has the same demethanizer at the up front s the C-E Lummus process fro the cracking of naphtha for the production of ethylene. The different for C-E Lumus from optimal distillation sequencing solution are without the unit of PSA and debutanizer (Figure 16).~~

The optimal distillation sequence obtained from our computational experiments using the CPI naphtha composition is compared against the configuration of Titan Petrochemical (M) Sdn. Bhd, which uses a similar feedstock of liquid naphtha. The major difference is that Titan's configuration uses a high pressure (HP) depropanizer at the front-end. According to Meyer (2005, p. 6.60), a front-end depropanizer is used when propane and heavier materials are the primary cracked feed.

On the other hand, our optimal configuration based on CPI's naphtha composition as the feed has demethanizer at the front-end, similar to the C-E Lummus naphtha cracking process configuration for ethylene production. However, compared to our configuration, the C-E Lummus topology does not include ~~an acetylene reactor, a~~ a PSA.~~, and an MAPD reactor.~~

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~~For the Titan Petrochemicals (M) Sdn.Bhd (Figure 15), the distillation configuration is different by using depropanizer at the front end. According to Meyer (2005), front end depropanizer is used when propane and heavier material is the primary cracked feed.~~

~~From the~~It is seen from our computational results that both forms of feed composition of typical gaseous ethane feedstock ~~,~~(such as that of EPEMSB) and typical~~ using feedstock of ethane from EPEMSB and~~ ~~feedstock of~~liquid naphtha feedstock (such as that of CPI (2005)) ~~from University of Manchester's Process Integration (2005)~~ generates~~yield~~ the same optimal configuration or topology of distillation sequencing.

5.2. Optimal and Suboptimal Distillation Sequences using Integer Cuts

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By incorporating ~~using~~ integer cuts, we can obtain the second best, ~~and the~~ third best, and subsequent "suboptimally best" –distillation configurations~~solutions~~ from ~~the MILP~~an integer program. According to Floudas and Paules (~~,~~–1988), ~~,~~ it is important to consider the restriction of the branch and bound enumeration tree for the solution of an integer program ~~is important in the solution of mathematical formulation~~. ~~From, the integer cuts, w~~We can thus compare the solutions in terms of ~~the annualized cost and the~~ total mass flow-rate. Integer cut is a

type of weak integer cut that could be derived are the ones that will ensure that those previously considered integer combinations cannot be encountered again. For the case when the integer combination is an element of some unit hypercube (i.e., binary variables), the following well-known integer cut will perform the above tasks.

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Lemma (Duran and Grossmann, 1986), Given any integer combination with index sets , s.t. $|B^i| + |NB^i| = m$, the integer constraint will be violated only by y_i and no other y_k 1 y^i. Note that $|B^j|$ is the number of terms in the first summation.

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5.2.1 Case 1: Ethane feedstock from Ethylene Polyethylene (M) Sdn. Bhd (EPEMSB)

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Table 12~~12~~~~11~~ Integer Cut for Ethane Gas Feedstock from EPEMSB

	Ethane Gas Feedstock					
	Best Solution	Flowrate -(ton/hr)	2nd Best Solution	Flowrate -(ton/hr)	3rd -Best Solution	Flowrate -(ton/hr)
Distillation Sequenc~~e~~ing	C1a	998.9	C1a	998.8	C1a	998.80
	C3a	746.803	C3a	746.803	C3a	746.803
	PSA	251.997	PSA	251.997	PSA	251.997
	R1a	700.576	C4a	700.576	R1a	700.576
	C8a	46.227	C8a	46.227	C8a	46.227
	R2	13.679	R2	13.679	R2	13.679

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	C11	13.679	C11	13.679	C11~~C12~~	13.679~~15.845~~
	C10	697.423	C10	697.423	C10~~R4~~	697.423~~16.704~~
	OCU	32.548	OCU	32.548	C9~~C11~~	32.548~~13.679~~
					C12~~C10~~	15.845~~697.423~~
					R4~~C9~~	16.704~~32.548~~
Total Mass Flowrate (ton/hr)		3501.832~~Total Mass Flow (ton/hr)~~		3501.832~~Total Mass Flow (ton/hr)~~		3534.281 ~~Total Mass Flow (ton/hr)~~
		~~3501.832~~		~~3501.832~~		~~3534.281~~

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Table ~~11~~ 12 lists~~shows~~ the optimal and suboptimal distillation sequences ~~integer cuts~~ for the feed composition of ethane gas feedstock for~~rom~~ EPEMSB. The optimal solution and second~~2nd~~ best solution involves~~show~~ lower~~the least~~ total mass flow-rate (3501.831 ton/hr) compared to the third ~~3rd~~ best solution, which is consistent with the heuristic of selecting the sequence with minimum total mass flow-rate.

By incorporating~~troducing~~ appropriate integer cuts as constraints in the model formulation, task R1a (acetylene catalytic hydrogenation reactor) is selected in the optimal solution~~,~~ while ~~the~~ task C4a (extractive distillation) is selected in the second best solution. According to ~~John~~ McK~~k~~etta and ~~William~~ Aaron (1984) in the authoritative McKetta's Encyclopedia of Chemical Processing and Design, if economically attractive, the acetylene may be recovered by extractive distillation. In most cases, it is simply hydrogenated to ethylene and ethane, which involves less equipment and a higher production of ethylene.

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5.2.2 Case 2: Naphtha Composition of~~from~~ ~~University of Manchester's Centre for Process Integration~~CPI (2005)

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Table 13~~13~~~~12~~ Integer cuts for naphtha liquid feedstock from University of Manchester's Centre for Process Integration (2005)

Naphtha Liquid Feedstock						
	Best Solution	Flow (ton/hr)	2^{nd} Best Solution	Flow(ton/hr)	3^{rd} Best Solution	Flow (ton/hr)
Distillation Sequenc~~ing~~	C1a	961.80	C1a	961.80	C1a	961.80
	C3a	800.025	C3a	800.025	C3a	800.025
	PSA	161.775	PSA	161.775	PSA	161.775
	R1a	339.709	R1a	339.709	R1a	339.709
	C8a	460.316	C8a	460.316	C8a	460.316
	R2	155.785	R2	155.785	R2	155.785
	C11	155.785	R4	211.061	R4~~R3~~	211.061~~93.470~~
	C10	322.674	C12	93.470	R3~~R4~~	93.470~~211.061~~
	OCU	304.531	C11	155.785	C11	155.785
			C10	332.674	C10	332.674
			C9	304.531	C9	304.531
Total Mass Flowrate (ton/hr)		3662.4~~Total Mass Flow (ton/hr)~~		3976.931~~Total Mass Flow (ton/hr)~~		3976.931~~Total Mass Flow (ton/hr)~~
		~~3662.4~~		~~3976.931~~		~~3976.931~~

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Table ~~12~~ 13 lists the optimal and suboptimal distillation sequences for the feed composition of ~~shows the integer cuts for~~ naphtha liquid feedstock from ~~University of Manchester's Centre for Process Integration~~ CPI (2005). ~~-~~The optimal sequence for the naphtha has the least total mass flow compared to the ~~than~~ ~~2^{nd}~~ second best and third~~3^{rd}~~ best solutions, although the two best suboptimal solutions share the same mass flowrate. However, note that the process design textbook by Biegler, Grossmann, and Westerberg (1997) has reported an example in which

~~Referring to Andrevoich and Westerburg (1985) who developed the superstructure which has network of four components, also shown that~~ the ~~3^{rd}~~ third best solution has a

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lower total mass flow-rate ~~(2250 kmol/hr)~~ than the second ~~2nd~~ best ~~soluti~~solution.~~on (2400 kmol/hr).~~

5.3 Computational Experiments

Table 1~~3~~4 summarizes the problem size and statistics on the performance of computational experiments conducted in this work.

Table 14~~1~~4~~13~~ Model size and c~~C~~omputational ~~statistics of problem size~~performance

Type of model	Mixed-integer linear programming (MILP)
Solver for MILP	CPLEX
No. of continuous variables	35
No. of binary variables	79
No. of constraints	142
No. of iterations	24

REMARKS ON COMPUTATIONAL EXPERIMENTS

~~☐~~Solution of the MILP model using GAMS/CPLEX that does not account for the split flows between selections of parallel tasks will select task R1c in its optimal sequence.

~~☐~~Also, ~~A~~assumption on 100% recovery is not accurate and impacts on the computational results.

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CHAPTER 5

CONCLUDING REMARKS~~SIONS~~ & RECOMMENDATIONS FOR FUTURE WORK

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5.1. CONCLUDING REMARKS

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The ~~In conclusion, i~~intermediate representation superstructure ha~~i~~s been employed~~used~~ to represent the optimization approaches and strategies for distillation separation for olefin production. According to Caballero and Grossman (~~, ~~1999), the intermediate representation superstructure has shown ~~a ~~good performance in reaching the global optimal solution. Furthermore, ~~intermediate representation~~this ~~ ~~superstructure form ~~will~~ involves less number of equations compared to STN representation superstructure.

A MILP model has been developed by representing the discrete and continuous variables for distillation sequencing for olefin production. By using different feedstocks, the computational results yield the same optimal sequencing. The optimal solution obtained is further validate by the most common heuristic which is the selection of column sequencing with least total mass flow rate.

5.2. RECOMMENDATIONS FOR FUTURE WORK

An immediate future work is to conduct more rigorous computational experiments in order to investigate the governing parameter, i.e., the most important parameter~~(~~s~~)~~ that determine~~s~~ the selection of the optimal distillation sequence. Feed composition does not appear to be the governing parameter. The logical constraints could be a probable governing constraint that is too restrictive in its formulation, although more work is required to validate this preliminary hypothesis.

A more representative model could be developed by incorporating thermodynamic limitations on the operating process conditions such as temperature and pressure and the inclusion of important physical parameters such as relative volatility in distillation column separation. As well, there are merits in considering the real-life features of ethylene plants such as the operations involving drying and chilling train at the front-end.

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.

Consideration of demand ~~and supply~~ constraints should be taken into account in the future work in order to integrate with the production planning and scheduling.

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APPENDICES I

GAMS CODE (Ethane/Naphtha)~~)~~

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GAMS Rev 146  x86/MS Windows                    06/03/06 22:29:18 Page 1
: Naphtha Separation
C o m p i l a t i o n


   3
   4
   5
*=========================================================================
=
      =====
   6  *Declaration of Sets
   7
*=========================================================================
=
      =====
   8  SETS
   9  *the set of all tasks in superstructure
  10
  11  T        Set of Task
  12  /
  13  OIL  Fractionator
  14  QUENCH  Fractionator
  15  FEED
  16  C1a,C1b,C1c
  17  C2a,C2b,C2c
  18  C3a,C3b,C3c
  19  PSA
  20  R1a,R1b,R1c
  21  C4a,C4b,C4c
  22  C8a,C8b
  23  R2,R3,R4
  24  C12,C11,C10,C9,C7,C6
  25  OCU
  26  C5a,C5b,C5c
  27
  28  /
  29
  30  U        Set of Unit-Equipment-Column associated with different task
  31  /
```

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```
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
/


pm(T,S)                    ! maps tasks to "Intermediate Product" streams( column produced)
/
(C1a,C2a,C6,C5a).ab
(C1b,C2b,C2c).ah
C1a.cl
(C1b,C3a).fl
C1c.ak
(C1c,C9).l
C2a.ck
(C2b,C3b).fk
(C2c,C3c,C8b,C9).jk
(C3a,C3b).ce
 C3c.ch
(R1a,C4a,C6,C7,C5b).cd
(R1b,C4b).ad_fh
(R1c,C4c,C5a).cd_fh
C5c.ad
(C5b,C5c,C7,C8a,C8b).fh
C8a.jl


/


fm(T,S)              !Set maps Unit to "Intermediate Product Feed" Streams- COlumn Directed
/
PSA.ab
(R1b,C4b).ah
C3a.cl
C8a.fl
(C2a,C2b,C2c).ak
R4.l
(C3b,C3c).ck
C8b.fk
(C12,R3).jk
(R1a,C4a).ce
(R1c,C4c).ch
```

```
C10.cd
(C5a,C5c).ad_fh
(C7,C5b).cd_fh
C6.ad
R2.fh
(C9,OCU).jl


/


task_producing_IP(T,S)   !Set for Logical Constraints for Structural task producing intermediate products
/
(C1a,C2a,C6,C5a).ab
C1c.ak
C1a.cl
C2a.ck
(C3a,C3b).ce
(C1b,C2b,C2c).ad_fh
C3c.cd_fh
C5c.cd
R2.fh
(C3a,C1b).fl
C8a.jl
(R1a,C4a,C7,C6,C5b).cd
(C9,C1c).l


/


IP_feed_to_task(T,S)    !Set for Logical Constraints for Structural Spec-Feed Source(From)
/
PSA.ab
C2a.ak
C2b.ak
C2c.ak
C3a.cl
C3b.ck
C3c.ck
(C4a,R1a).ce
(C4b,R1b).ad_fh
(C4c,R1c).cd_fh
C6.cd
C11.fh
C8a.fl

(C9,OCU).jl
```

```
128  C10.cd
129  R4.l
130
131  /
132
133
134  outlet_column(T,S)
135  /
136  PSA.ab,C3a.cl
137  (R1b,C4b).ah,C8a.fl
138  (C2a,C2b,C2c).ak,R4.l
139  (C3b,C3c).ck
140  C8b.fk
141  C12.jk
142  (R1a,C4a).ce
143  (R1c,C4c).ch,(R3).jk
144  C10.cd,(C5a,C5c).ad_fh,C5b.cd_fh
145  R2.fh,C6.ad
146  (OCU,C9).jl
147
148
149
150  /
151
152  column(T,S)
153  /
154  C1a.(ab,cl)
155  C1b.(ah,fl)
156  C1c.(ak,l)
157  C2a.(ab,ck)
158  C2b.(ah,fk)
159  C2c.(ah,jk)
160  C3a.(ce,fl)
161  C3b.(ce,fk)
162  C3c.(ch,jk)
163  (C4a,R1a).(cd)
164  (C4b,R1b).(ad_fh)
165  (C4c,R1c).(cd_fh)
166  C5a.(ab)
167  C5b.(cd,fh)
168  C5c.(ad,fh)
169  C6.(ab,cd)
170  C7.(cd,fh)
171  C8a.(fh,jl)
172  C8b.(fh,jk)
173  C9.(jk,l)
174
175
176  /
177
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```
 178
 179
 180  ;
 181
 182
 183
 184  ALIAS (S,S1);
 185  AlIAS (T,T1);
 186
*=======================================================================
=
     ======
 187  *Declaration of Parameters for rest of model
 188
*=======================================================================
=
     ======
 189  PARAMETER
 190
 191  M(T)   Big M Constant-1000 is the upper bound as it corresponds to the fee
     d flow rate of the intial mixture;
 192
 193  M(T)=1000;
 194
 195  PARAMETER
 196
 197  spltfrc(T,S)       Split Fraction maps to unit to Intermediate Product str
     eams
 198  /
 199  QUENCH_FRACTIONATOR.al   0.9988,
 200  OIL_FRACTIONATOR.m       0.0012,
 201  C1a.ab           0.2523,
 202  C1a.cl           0.7477,
 203  C1b.ah           0.9798,
 204  C1b.fl           0.0202,
 205  C1c.ak           0.9833,
 206  C1c.l            0.0167,
 207  C2a.ab           0.2566,
 208  C2a.ck           0.7434,
 209  C2b.ah           0.9883,
 210  C2b.fk           0.0117,
 211  C2c.ah           0.9839,
 212  C2c.jk           0.0161,
 213  C3a.ce           0.9381,
 214  C3a.fl           0.0619,
 215  C3b.ce           0.9596,
 216  C3b.fk           0.0404,
 217  C3c.ch           0.9783,
 218  C3c.jk           0.0217,
 219  C4a.cd           0.9955,
```

```
C4b.ad_fh       0.9967,
C4c.cd_fh       0.9955,
C5a.ab          0.2617,
C5a.cd_fh       0.7383,
C5b.cd          0.9808,
C5b.fh          0.0192,
C5c.ad          0.9858,
C5c.fh          0.0142,
R1a.cd          0.9955,
R1b.ad_fh       0.9967,
R1c.cd_fh       0.9955,
C8a.fh          0.2959,
C8a.jl          0.7041,
C8b.fh          0.4633,
C8b.jk          0.5367,
C6.ab           0.2655,
C6.cd           0.7345,
C9.jk           0.4868,
C9.l            0.5132,
C7.cd           0.9808,
C7.fh           0.0192



/

*Ethylene Production = 450 kT/year
Fixed_Cost(T)       Fixed Cost per year (for ethane: 56 $ per ton C2H4 in
    Middle East)
Operating_Cost(T)   Operating Cost or total production cost(140 $ per ton
    C2H4 in Middle East)
;

Fixed_Cost(T) = 56000;    #(in unit of $/year)
Operating_Cost(T) = 140000;
;




*=========================================================================
=
    ======
*Define scalar quantities for rest of model

*=========================================================================
=
    ======

SCALARS

```

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```
 262  TOTFEED  total feed flow rate(feedstock in tonnage) to superstructure   /1
      000/ ;
 263  *646
 264
 265
*=======================================================================
=
      ======
 266  *Declaration of variables
 267
*=======================================================================
=
      ======
 268  VARIABLE
 269  Z        Objective function
 270
 271  ;
 272
 273  BINARY VARIABLES
 274  Y(T)      Columns selection in superstruture associated with T Tasks(exist
      ance Or Non-existance)
 275  ;
 276
 277  POSITIVE VARIABLES
 278  F(T)      Flow Rate of selected T task associated with S streams
 279  Fraction(T)
 280  ;
 281
 282
*=======================================================================
=
      ======
 283  *Declaration of Equations
 284
*=======================================================================
=
      ======
 285  *for material balances around unit, mixers, splitters
 286  *for logical constraitns on design specifications, structural specificatio
      ns.
 287  *for switching constraints
 288
 289  EQUATIONS
 290  OBJECTIVE        Objective function
 291  TotalFeed, Oil,Feed_Column
 292  Initial_FEED     Initial Column_Feed to superstructure
 293
 294  MB_Unit          Material Balances for Unit
 295  MB_C11
 296
```

```



*SPLIT1,SPLIT2,SPLIT3,SPLIT4,SPLIT5,SPLIT6,SPLIT7,SPLIT8

DS1
DS2
DS3
DS4
DS5
DS6a,DS6b,DS6c
DS7,
DS9
DS8



Inlet(T,S)        Inlet Condition
InletC5a,InletC5b,InletC5c,InletC7,InletR2,InletC8b

STRUCTURAL_SPEC_LC(T,S)  Overhead & Bottom
SP_C5a
BigM            Big M Logical Constraints-Switching Constraints with T tasks
*INTEGER_CUT_1
*$ontext
*CUTS_2nd_Optimum
*CUTS_3rd_Optimum
*$offtext
;

********Objective Function*******************************************************
*OBJECTIVE..     Z=E= SUM(T, Capital_Cost(T)*SUM(T,F(T));
OBJECTIVE..      Z=E= SUM(T,Fixed_Cost(T)*Y(T)) + SUM(T,Operating_Cost(T)*F(T));



*Initial Feed to Superstructure

TotalFeed..      TOTFEED =E= spltfrc('QUENCH_FRACTIONATOR','al')*F('QUENCH_FRACTIONATOR') + spltfrc('OIL_FRACTIONATOR','m')*F('OIL_FRACTIONATOR');


Oil..            F('OIL_FRACTIONATOR')=E= (TOTFEED-F('FEED'))/ spltfrc('OIL_FRACTIONATOR','m');
*Cannot find the flow rate of Oil Fractionaor

Feed_Column..    spltfrc('QUENCH_FRACTIONATOR','al')*F('QUENCH_FRACTIONATOR')-F('FEED')=E=0;
```

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Initial_FEED..   F('FEED') =E= F('C1a')+ F('C1b')+F('C1c');
 
 
*Unit/Task
MB_Unit(S)..    SUM(T$pm(T,S), spltfrc(T,S)*F(T)) =E= SUM(T $ fm(T,S),F(T)
 );
 
MB_C11..        F('R2')=E=F('C11');
 
 
    SPLIT1..     F('R1c') =E= Fraction('R1c')*spltfrc('C3c','ch')*F('C3c');

    SPLIT2..     F('C4c') =E= Fraction('C4c')*spltfrc('C3c','ch')*F('C3c');

    SPLIT3..     F('R1b') =E= Fraction('R1b')*(spltfrc('C1b','ah')*F('C1b') +
    spltfrc('C2b','ah')*F('C2b') + spltfrc('C2c','ah')*F('C2c'));

    SPLIT4..     F('C4b') =E= Fraction('C4b')*(spltfrc('C1b','ah')*F('C1b') +
    spltfrc('C2b','ah')*F('C2b') + spltfrc('C2c','ah')*F('C2c'));

    SPLIT5..     F('R1a') =E= Fraction('R1a')*(spltfrc('C3a','ce')*F('C3a') +
    spltfrc('C3b','ce')*F('C3b'));

    SPLIT6..     F('C4a') =E= Fraction('C4a')*(spltfrc('C3a','ce')*F('C3a') +
    spltfrc('C3b','ce')*F('C3b'));

    SPLIT7..     F('R3')=E= Fraction('R3')*(spltfrc('C2c','jk')*F('C2c') + spl
    tfrc('C3c','jk')*F('C3c') + spltfrc('C8b','jk')*F('C8b') + spltfrc('C9','j
    k')*F('C9'));

    SPLIT8..     F('C12')=E= Fraction('C12')*(spltfrc('C2c','jk')*F('C2c') + s
    pltfrc('C3c','jk')*F('C3c') + spltfrc('C8b','jk')*F('C8b') + spltfrc('C9',
    'jk')*F('C9'));
 
 
*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')+Y('R1c')=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;
DS6c..    Y('R1c')+ Y('C4c')=L=2;
```

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*No more than 1 process allowed( none or 1 process selected)
DS7..     Y('C5a')+ Y('C5b')+ Y('C5c')=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);

*Limit Choice of Overhead & Bottom
STRUCTURAL_SPEC_LC(T,S)$column(T,S)..   SUM(T1 $ outlet_column(T1,S), Y(T1
   ) )- Y(T) =G= 0;

SP_C5a..                              Y('C7')-Y('C5a') =G=0;


*Inlet Condition
Inlet(T,S) $ IP_feed_to_task(T,S)..     SUM( T1 $ task_producing_IP(T1,S),
    Y(T1) ) - Y(T) =G= 0;

InletC5a..                          Y('C4b')+Y('R1b')-Y('C5a')=G=0;
InletC5b..                          Y('C4c')+ Y('R1c') -Y('C5b')=G=0;
InletC5c..                          Y('C4b')+Y('R1b')-Y('C5c')=G=0;

InletC7..                           Y('C5a')-Y('C7')=G=0;
InletR2..                           Y('C5b')+Y('C5c')+Y('C7')+Y('C8a')
   +Y('C8b')-Y('R2')=G=0;

InletC8b..                          Y('C3b')+Y('C2b')-Y('C8b')=G=0;

*Integer Cuts to obtain second best solution
*CUTS_2nd_Optimum..                Y('OIL_Fractionator') + Y('QUENCH_
   Fractionator')+ Y('FEED')+Y('C1a') + Y('C3a')+Y('PSA')+Y('R1a')+Y('C8a')+Y
   ('R2')+Y('C11')+Y('C10')+Y('OCU')=L= 11 ;

*Integer Cuts to obtain 3rd best solution
*CUTS_3rd_Optimum..                Y('OIL_Fractionator') + Y('QUENCH_
   Fractionator')+ Y('FEED')+Y('C1a')+ Y('C3a')+ Y('PSA')+Y('C4A')+Y('C8a')+Y
   ('R2')+Y('C11')+Y('C10')+Y('OCU')=L=11 ;


*Integer Cuts to obtain second best solution
*Cuts(k)..              sum(T, sign(ycolk(T,k)-0.5)*Y(T)) =l= sum(T,ycol
   k(T,k)) - 1;


```

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```
*sum(i,sign(ycolk(i,k)-0.5)*ycol(i)) =l= sum(i,ycolk(i,k)) - 1;
*INTEGER_CUT_1..     Y('OIL_Fractionator') + Y('QUENCH_Fractionator') + Y(
     'FEED') + Y('C1c') + Y('C2a') + Y('C3c') + Y('C5b') + Y('PSA') + Y('R1c')
     + Y('C4c') + Y('R2') + Y('R3') + Y('R4') + Y('C10') + Y('C11') + Y('C12')
     + Y('C13') =L= 15;


      Y('C13')-Y('R4')=G=0;            directed      SP
      Y('R4')-Y('C13')=G=0;            inlet of C13

      Y('C14')-Y('C13')=G=0;           bottom        SP
      Y('C13')-Y('C14')=G=0;           inlet of C14

      Y('C15')-Y('C14')=G=0;           bottom       SP
      Y('C14')-Y('C15')=G=0;           inlet of C15

      Y('C16')-Y('C15')=G=0;           bottom        SP
      Y('C15')-Y('C16')=G=0;           inlet of C16

      Y('R5')-Y('C16')=G=0;            top         SP
      Y('C16')-Y('R5')=G=0;            inlet of R5

      Y('C17')-Y('R5')=G=0;           directed       SP
      Y('R5')-Y('C17')=G=0;           inlet of C17

      Y('C18')-Y('C17')=G=0;           bottom       SP
      Y('C17')-Y('C18')=G=0;           inlet of C18

      Y('C18')-Y('C19')=G=0;           inlet C19
      Y('C20')-Y('C19')=G=0;                SP

      Y('C19')-Y('C18')=G=0;     overhead         SP
      Y('C20')-Y('C18')=G=0;     bottom           SP


      Y('C18')+Y('C19') -Y('C20')=G=0;    inlet of C20

      Y('C21')-Y('C20')=G=0;           directed       SP
      Y('C20')-Y('C21')=G=0;          inlet of C21


 ;



 MODEL NAPHTHA
 /
 ALL

 /;
```

```
 475
 476  *Intial values and bound are given to avoid getting stuck at an infeasible
      point wen the NLP solver starts up
 477
 478
 479  F.up(T)=TOTFEED;
 480  Y.up(T)=1;
 481
 482
 483  Fraction.LO(T) = 0.00;
 484  Fraction.UP(T) = 1.00;
 485
 486
 487  *OPTION
 488  OPTION
 489  *MINLP = BARON
 490  MIP = CPLEX
 491  *MINLP = SBB
 492  *MINLP = DICOPT     # DICOPT returns infeasible solution to this problem
 493  LIMROW = 0
 494  LIMCOL = 0
 495  ;
 496
 497
 498
 499
 500
 501  SOLVE NAPHTHA USING MIP MINIMIZING Z
 502  ;
 503
 504  DISPLAY Z.L, Y.L, F.L;


COMPILATION TIME     =        0.010 SECONDS      3 Mb  WIN223-146 Nov 21, 2006
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GAMS Rev 146  x86/MS Windows                    06/03/06 22:29:18 Page 2
: Naphtha Separation
Model Statistics    SOLVE NAPHTHA Using MIP From line 501


MODEL STATISTICS

BLOCKS OF EQUATIONS          28     SINGLE EQUATIONS          134
BLOCKS OF VARIABLES           3     SINGLE VARIABLES           69
NON ZERO ELEMENTS           419     DISCRETE VARIABLES         34


GENERATION TIME      =        0.010 SECONDS      4 Mb  WIN223-146 Nov 21, 2006


EXECUTION TIME       =        0.020 SECONDS      4 Mb  WIN223-146 Nov 21, 2006
```

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GAMS Rev 146  x86/MS Windows                    06/03/06 22:29:18 Page 3
: Naphtha Separation
Solution Report     SOLVE NAPHTHA Using MIP From line 501


               S O L V E      S U M M A R Y

     MODEL   NAPHTHA             OBJECTIVE  Z
     TYPE    MIP                 DIRECTION  MINIMIZE
     SOLVER  CPLEX               FROM LINE  501

**** SOLVER STATUS     1 NORMAL COMPLETION
**** MODEL STATUS      8 INTEGER SOLUTION
**** OBJECTIVE VALUE        910746413.5937

 RESOURCE USAGE, LIMIT          0.240      1000.000
 ITERATION COUNT, LIMIT        24         10000

GAMS/Cplex    Nov 27, 2006 WIN.CP.CP 22.3 032.035.041.VIS For Cplex 10.1
Cplex 10.1.0, GAMS Link 32

Solution satisfies tolerances.

MIP Solution:    910746413.593735    (24 iterations, 0 nodes)
Final Solve:     910746413.593724    (0 iterations)

Best possible:   910682452.747934
Absolute gap:        63960.845801
Relative gap:            0.000070


                       LOWER     LEVEL     UPPER    MARGINAL

---- EQU OBJECTIVE       .         .         .        1.000
---- EQU TotalFeed  -1000.000 -1000.000 -1000.000 -1.160E+8
---- EQU Oil        8.3333E+5 8.3333E+5 8.3333E+5   756.998
---- EQU Feed_Colu~      .         .         .         .
---- EQU Initial_F~      .         .         .    -4.908E+5

  OBJECTIVE  Objective function
  Initial_FEED  Initial Column  Feed to superstructure

---- EQU MB_Unit  Material Balances for Unit

         LOWER     LEVEL     UPPER    MARGINAL

ab         .         .         .    -1.400E+5
cl         .         .         .    -4.220E+5
ah         .         .         .         .
fl         .         .         .    -3.214E+5
```

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```
ak          .          .          .          .
l           .          .          .          .
ck          .          .          .          .
fk          .          .          .          .
jk          .          .          .          .
ce          .          .          .    -2.794E+5
ch          .          .          .          .
cd          .          .          .    -1.400E+5
ad_fh       .          .          .          .
cd_fh       .          .          .          .
ad          .          .          .          .
fh          .          .          .    -2.800E+5
jl          .          .          .    -1.400E+5

                     LOWER     LEVEL     UPPER    MARGINAL

---- EQU MB_C11          .          .          .    -1.400E+5
---- EQU DS1          1.000      1.000      1.000        .
---- EQU DS2           -INF        .        1.000        .
---- EQU DS3           -INF      1.000      1.000        .
---- EQU DS4           -INF      1.000      1.000        .
---- EQU DS5           -INF        .        1.000        .
---- EQU DS6a          -INF      1.000      2.000        .
---- EQU DS6b          -INF        .        2.000        .
---- EQU DS6c          -INF        .        2.000        .
---- EQU DS7           -INF        .        1.000        .
---- EQU DS9           -INF        .        2.000        .
---- EQU DS8           -INF      1.000      1.000        .

---- EQU Inlet  Inlet Condition

            LOWER     LEVEL     UPPER    MARGINAL

C2a.ak          .          .        +INF          .
C2b.ak          .          .        +INF          .
C2c.ak          .          .        +INF          .
C3a.cl          .          .        +INF          .
C3b.ck          .          .        +INF          .
C3c.ck          .          .        +INF          .
PSA.ab          .          .        +INF          .
R1a.ce          .          .        +INF          .
R1b.ad_fh       .          .        +INF          .
R1c.cd_fh       .          .        +INF          .
C4a.ce          .        1.000      +INF          .
C4b.ad_fh       .          .        +INF          .
C4c.cd_fh       .          .        +INF          .
C8a.fl          .          .        +INF          .
R4 .l           .          .        +INF          .
C11.fh          .          .        +INF          .
C10.cd          .          .        +INF          .
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C9 .jl         .        1.000     +INF        .
C6 .cd          .        1.000     +INF        .
OCU.jl          .          .        +INF        .

                    LOWER     LEVEL     UPPER    MARGINAL

---- EQU InletC5a          .          .        +INF        .
---- EQU InletC5b          .          .        +INF        .
---- EQU InletC5c          .          .        +INF        .
---- EQU InletC7           .          .        +INF        .
---- EQU InletR2           .          .        +INF        .
---- EQU InletC8b          .          .        +INF        .

---- EQU STRUCTURAL_SPEC_LC  Overhead & Bottom

           LOWER     LEVEL     UPPER    MARGINAL

C1a.ab          .          .        +INF        .
C1a.cl          .          .        +INF        .
C1b.ah          .          .        +INF        .
C1b.fl          .        1.000     +INF        .
C1c.ak          .          .        +INF        .
C1c.l           .          .        +INF        .
C2a.ab          .        1.000     +INF        .
C2a.ck          .          .        +INF        .
C2b.ah          .          .        +INF        .
C2b.fk          .          .        +INF        .
C2c.ah          .          .        +INF        .
C2c.jk          .          .        +INF        .
C3a.fl          .          .        +INF        .
C3a.ce          .          .        +INF        .
C3b.fk          .          .        +INF        .
C3b.ce          .        1.000     +INF        .
C3c.jk          .          .        +INF        .
C3c.ch          .          .        +INF        .
R1a.cd          .          .        +INF        .
R1b.ad_fh       .          .        +INF        .
R1c.cd_fh       .          .        +INF        .
C4a.cd          .        1.000     +INF        .
C4b.ad_fh       .          .        +INF        .
C4c.cd_fh       .          .        +INF        .
C8a.fh          .          .        +INF        .
C8a.jl          .          .        +INF        .
C8b.jk          .          .        +INF        .
C8b.fh          .        1.000     +INF        .
C9 .l           .          .        +INF        .
C9 .jk          .          .        +INF        .
C7 .cd          .        1.000     +INF        .
C7 .fh          .        1.000     +INF        .
C6 .ab          .        1.000     +INF        .
```

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```
C6 .cd          .        1.000     +INF       .
C5a.ab          .        1.000     +INF       .
C5b.cd          .        1.000     +INF       .
C5b.fh          .        1.000     +INF       .
C5c.ad          .          .       +INF       .
C5c.fh          .        1.000     +INF       .

                LOWER     LEVEL     UPPER    MARGINAL

---- EQU SP_C5a           .         .       +INF       .

---- EQU BigM  Big M Logical Constraints-Switching Constraints with T tasks

                LOWER     LEVEL     UPPER    MARGINAL

OIL_Fractionator        -INF        .         .         .
QUENCH_Fractionator     -INF        .         .         .
FEED                    -INF     -1.200       .         .
C1a                     -INF     -1.200       .         .
C1b                     -INF        .         .    -3.443E+5
C1c                     -INF        .         .    -3.508E+5
C2a                     -INF        .         .         .
C2b                     -INF        .         .         .
C2c                     -INF        .         .         .
C3a                     -INF   -253.197       .         .
C3b                     -INF        .         .         .
C3c                     -INF        .         .         .
PSA                     -INF   -748.003       .         .
R1a                     -INF   -299.424       .         .
R1b                     -INF        .         .         .
R1c                     -INF        .         .         .
C4a                     -INF        .         .         .
C4b                     -INF        .         .         .
C4c                     -INF        .         .         .
C8a                     -INF   -953.773       .         .
C8b                     -INF        .         .         .
R2                      -INF   -986.321       .         .
R3                      -INF        .         .         .
R4                      -INF        .         .         .
C12                     -INF        .         .         .
C11                     -INF   -986.321       .         .
C10                     -INF   -302.577       .         .
C9                      -INF        .         .         .
C7                      -INF        .         .         .
C6                      -INF        .         .         .
OCU                     -INF   -967.452       .         .
C5a                     -INF        .         .         .
C5b                     -INF        .         .         .
C5c                     -INF        .         .         .
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               LOWER     LEVEL     UPPER    MARGINAL

---- VAR Z             -INF  9.1075E+8     +INF       .

  Z  Objective function

---- VAR Y  Columns selection in superstruture associated with T Tasks(existance
            Or Non-existance)

               LOWER     LEVEL     UPPER    MARGINAL

OIL_Fractionator         .         1.000     1.000 56000.000
QUENCH_Fractionator      .         1.000     1.000 56000.000
FEED                     .         1.000     1.000 56000.000
C1a                      .         1.000     1.000 56000.000
C1b                      .          .        1.000 -3.443E+8
C1c                      .          .        1.000 -3.508E+8
C2a                      .          .        1.000 56000.000
C2b                      .          .        1.000 56000.000
C2c                      .          .        1.000 56000.000
C3a                      .         1.000     1.000 56000.000
C3b                      .          .        1.000 56000.000
C3c                      .          .        1.000 56000.000
PSA                      .         1.000     1.000 56000.000
R1a                      .         1.000     1.000 56000.000
R1b                      .          .        1.000 56000.000
R1c                      .          .        1.000 56000.000
C4a                      .          .        1.000 56000.000
C4b                      .          .        1.000 56000.000
C4c                      .          .        1.000 56000.000
C8a                      .         1.000     1.000 56000.000
C8b                      .          .        1.000 56000.000
R2                       .         1.000     1.000 56000.000
R3                       .          .        1.000 56000.000
R4                       .          .        1.000 56000.000
C12                      .          .        1.000 56000.000
C11                      .         1.000     1.000 56000.000
C10                      .         1.000     1.000 56000.000
C9                       .          .        1.000 56000.000
C7                       .          .        1.000 56000.000
C6                       .          .        1.000 56000.000
OCU                      .         1.000     1.000 56000.000
C5a                      .          .        1.000 56000.000
C5b                      .          .        1.000 56000.000
C5c                      .          .        1.000 56000.000

---- VAR F  Flow Rate of selected T task associated with S streams

               LOWER     LEVEL     UPPER    MARGINAL
```

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```
OIL_Fractionator         .     1000.000  1000.000      .
QUENCH_Fractionator      .     1000.000  1000.000 -1.158E+8
FEED                     .      998.800  1000.000      .
C1a                      .      998.800  1000.000      .
C1b                      .         .     1000.000      .
C1c                      .         .     1000.000      .
C2a                      .         .     1000.000 1.7592E+5
C2b                      .         .     1000.000 1.4000E+5
C2c                      .         .     1000.000 1.4000E+5
C3a                      .      746.803  1000.000      .
C3b                      .         .     1000.000 4.0808E+5
C3c                      .         .     1000.000 1.4000E+5
PSA                      .      251.997  1000.000      .
R1a                      .      700.576  1000.000      .
R1b                      .         .     1000.000 1.4000E+5
R1c                      .         .     1000.000 1.4000E+5
C4a                      .         .     1000.000 7.219E-12
C4b                      .         .     1000.000 1.4000E+5
C4c                      .         .     1000.000 1.4000E+5
C8a                      .       46.227  1000.000      .
C8b                      .         .     1000.000 2.6972E+5
R2                       .       13.679  1000.000      .
R3                       .         .     1000.000 1.4000E+5
R4                       .         .     1000.000 1.4000E+5
C12                      .         .     1000.000 1.4000E+5
C11                      .       13.679  1000.000      .
C10                      .      697.423  1000.000      .
C9                       .         .     1000.000      EPS
C7                       .         .     1000.000 2.8269E+5
C6                       .         .     1000.000 2.8000E+5
OCU                      .       32.548  1000.000      .
C5a                      .         .     1000.000 1.7664E+5
C5b                      .         .     1000.000 2.8269E+5
C5c                      .         .     1000.000 1.4398E+5


**** REPORT SUMMARY :        0     NONOPT
                             0 INFEASIBLE
                             0  UNBOUNDED
```

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```
GAMS Rev 146  x86/MS Windows                    06/03/06 22:29:18 Page 4
; Naphtha Separation
E x e c u t i o n


----    504 VARIABLE Z.L                =  9.107464E+8  Objective function

----    504 VARIABLE Y.L  Columns selection in superstruture associated with T T
                          asks(existance Or Non-existance)

OIL_Fractionator    1.000,    QUENCH_Fractionator 1.000
FEED                1.000,    C1a                 1.000
C3a                 1.000,    PSA                 1.000
R1a                 1.000,    C8a                 1.000
R2                  1.000,    C11                 1.000
C10                 1.000,    OCU                 1.000


----    504 VARIABLE F.L  Flow Rate of selected T task associated with S streams

OIL_Fractionator    1000.000,    QUENCH_Fractionator 1000.000
FEED                 998.800,    C1a                  998.800
C3a                  746.803,    PSA                  251.997
R1a                  700.576,    C8a                   46.227
R2                    13.679,    C11                   13.679
C10                  697.423,    OCU                   32.548



EXECUTION TIME       =        0.010 SECONDS      3 Mb  WIN223-146 Nov 21, 2006


USER: course license                                S060628:0842AL-WIN
      Phd course about mathematical programming              DC5953
      License for teaching and research at degree granting institutions


**** FILE SUMMARY

Input      C:\Documents and Settings\leesufen\Desktop\May_FYP\Ethane_EPMS_24May.
           gms
Output     C:\Documents and Settings\leesufen\My Documents\gamsdir\projdir\Ethan
           e_EPMS_24May.lst
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~~APPENDICES II~~

~~GAMS CODE (NAPHTHA)~~

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