OPTIMIZATION OF THE DEBUTANIZER IN A PLATFORMING UNIT USING PRO/II

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หัวข้อวิทยานิพนธ์	การหาสภาวะที่เหมาะสมของหอกลั่นแยกบิวเทนในหน่วยเพิ่มค่าออกเทนด้วยตัวเร่งปฏิกิริยาโดยใช้โปรแกรม PRO/II
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บทคัดย่อ

งานวิจัยนี้เสนอแบบจำลองและหาสภาวะการดำเนินงานที่เหมาะสมสำหรับหอกลั่นแยกบิวเทนในหน่วยเพิ่มค่าออกเทนด้วยตัวเร่งปฏิกิริยาของโรงกลั่นน้ำมันโดยใช้โปรแกรม PRO/II การหาจุดปฏิบัติงานที่เหมาะสมเพื่อให้ได้ผลตอบแทนสูงสุดภายใต้เงื่อนไขตามคุณภาพของผลิตภัณฑ์ทำโดยปรับพารามิเตอร์ คือ ความดันของหอกลั่นและพลังงานของรีบอยเลอร์ การสร้างแบบจำลองใช้โปรแกรม PRO/II คุณสมบัติและข้อมูลจริงจากการปฏิบัติงานของหอกลั่นแยกบิวเทนช่วงสภาวะคงตัว (Steady state) พบว่าการจำลองด้วยแบบจำลองพื้นฐานสอดคล้องกับข้อมูลการปฏิบัติงานจริงที่ได้จากหอกลั่น และจากการประเมินทางเศรษฐศาสตร์เบื้องต้นได้ผลตอบแทนสูงสุดที่ 61.12 เหรียญสหรัฐต่อชั่วโมงที่ความดันของหอกลั่น 14.5 กิโลกรัมต่อตารางเซ็นติเมตร และพลังงานของรีบอยเลอร์ที่ 3.2364 ล้านกิโลแคลอรีต่อชั่วโมงหรือที่เรียกว่ากรณี Relaxed reformate RVP เมื่อค่าความดันไอของรีฟอร์เมตที่อุณหภูมิ 60 องศาฟาเรนไฮต์ (Reid vapor pressure: RVP) ไม่เกิน 5.22 ปอนด์ต่อตารางนิ้ว สภาวะนี้มีความเหมาะสมที่จะเป็นแนวทางสำหรับกระบวนการผลิต นอกจากนี้การศึกษาผลกระทบของอุณหภูมิของเทรย์ที่ 8 พบว่าอุณหภูมิที่เพิ่มขึ้นทำให้ปริมาณ C_5^+ ในก๊าซปิโตรเลียมเหลวเพิ่มขึ้นอย่างชัดเจนแต่ไม่มีผลต่อความดันไอของรีฟอร์เมตที่อุณหภูมิ 60 องศาฟาเรนไฮต์

Thesis Title	Optimization of the debutanizer in a platforming unit using PRO/II
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ABSTRACT

This work presents the simulation model and the optimization of the operating conditions for a debutanizer of a platforming unit in a refinery plant using PRO/II simulation software. The optimal operating conditions for most profit based on product quality constraints were taken by varying the debutanizer column pressure and reboiler heat duty. The simulation model was simulated using PRO/II and the actual characteristic data of the debutanizer under steady state operation. The simulation results of the base case are found to agree well with the actual operating data. According to the preliminary economic evaluation by the optimization at the debutanizer column pressure of 14.5 kg/cm^2 and reboiler heat duty of 3.2364×10^6 kcal/h or so-called a relaxed reformate RVP case (at max. reformate Reid vapor pressure at 60 °F of 5.22 psi), the greatest economic benefit of 61.12 US$/h was obtained. This case was verified as a production guidelines. In addition, it was found that with an increase in the 8th-tray's temperature, the amount of C_5^+ in liquefied petroleum gas (LPG) significantly increased with no effect on reformate Reid vapor pressure at 60 °F.

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Nomenclatures

Latin capital and lowercase letters

a, b	Constants in Van der Waals equation; constants in Redlich-Kwong equation; constants in Soave-Redlich-Kwong equation
B	Flowrate of bottom product
D	Flowrate of distillate; fraction of selected key in the distillate product
F	Flowrate of feed
HY Key	Fraction of the selected heavy key
K_{ij}	Binary interaction parameters between different components
K_{LT} *Key*	Equilibrium constant of the light key component
K_{HY} *Key*	Equilibrium constant of the heavy key component
L	Flowrate of liquid; liquid flowrate in rectifying section
$\bar{L}$	Liquid flowrate in stripping section
LT Key	Fraction of the selected light key
n	Numbers of stages above feed stage
N_{m+1}	Minimum number of theoretical trays
m	Numbers of stages below feed stage
P	Pressure
P_C	Critical pressure
q	Rate of heat transfer
q^{-C}	Heat removed from the condenser
q^{-S}	Heat added at the reboiler
R	Universal gas constant; reflux ratio
T	Temperature
T_C	Critical temperature
V	Flowrate of vapor; vapor flowrate in rectifying section
$\bar{V}$	Vapor flowrate in stripping section

Nomenclatures (cont.)

V^T	Vapor from the top of the column to a condenser
W	Fraction of selected key in the bottom product
x	Mole fraction of liquid phase
y	Mole fraction of vapor phase
Greek letter	
α_{ij}	Relative volatility, component i relative to component j

Technical Abbreviations

ACN	Acetonitrile
ASTM	American Society for Testing and Materials
ATK	Aviation turbine kerosene
BK-10	Braun K-10
CCR	Continuous Catalyst Regeneration
DCO	Decant oil
EOS	Equations of state
FO	Fuel oil
GRK	Generic Redlich-Kwong
GS	Grayson-Streed
HAGO	Heavy atmospheric gas oil
HCN	Heavy cracked naphtha
HDO	Heavy diesel oil
HSD	High speed diesel
HSR	Heavy straight run
HVGO	Heavy vacuum gas oil
H_2S	Hydrogen sulfide gas
IGS	Improved Grayson-Streed
KSD	Kilobarrel per day
LACT	Liquid activity
LCGO	Light cycle gas oil
LCN	Light cracked naphtha
LDO	Light diesel oil
LPG	Liquefied petroleum gas
LSR	Light straight run
LVGO	Light vacuum gas oil

Technical Abbreviations (cont.)

MCN	Medium cracked naphtha
NHTU	Naphtha hydrotreating unit
NRTL	Non-random two-liquid equation
PR	Peng-Robinson
RVP	Reid vapor pressure
SRK	Soave-Redlich-Kwong
TBP	True boiling point
ULG	Unleaded gasoline
UNIFAC	Universal quasichemical functional group activity coefficient
UNIQUAC	Universal quasichemical
VHVGO	Very heavy vacuum gas oil
VLE	Vapor-liquid equilibrium
VR	Vacuum residue

Chapter 1

Introduction

1.1 Rationale

Industry and energy consumption in Thailand are growing; thus, the demands for petroleum feed fuels are rising. To satisfy the demands, many oil refineries have been trying to gain their profit or product margin from the existing units; however, sometimes process limitations occur in refinery. The conversion unit such as a platforming unit or catalytic reforming unit is usually considered for operational strategy or optimization.

Either production of reformate or liquefied petroleum gas (LPG) has become more attractive due to the increase in market demands. In the refinery plant, most of the reformate comes from the platforming unit. Off gas and LPG are the reaction by-products. The platforming unit consists of the reforming reactor and the debutanizer. The debutanizer separates reactor products into three streams, which are off gas, LPG and reformate. The production of reformate is about 20 times of LPG [1].

The present paper is focused on the separation of LPG and reformate. Off gas goes to the refinery fuel gas pool. The in spec LPG goes to LPG product tanks. Reformate is the main gasoline blending component. A simplified diagram of the debutanizer is shown in Figure 1.1. In this work, the debutanizer is a sieve-tray distillation column, which contains 32 actual trays including condenser and reboiler. Although the debutanizer is operated smoothly, it may not achieve the highest economic benefit. Optimization of the operating conditions at the debutanizer is approached to maximize the economic benefit [2]. The debutanizer is simulated by PRO/II software to find the operating condition guidelines for the maximum economic benefit, which is focused on LPG and/or reformate. PRO/II is a comprehensive computer simulation program that models the steady-state conditions of chemical processes. It helps engineers design a new process or analyze an existing operating unit.

The parameters to be optimized at the debutanizer are column pressure and reboiler temperature in terms of reboiler heat duty. The goal of the optimization in this work is determining the column pressure and reboiler heat duty of the debutanizer that give higher economic benefit as the maximum yields of LPG and/or reformate. The operating condition guidelines, which give higher benefits, can be selected from the optimization results.

The simulation model obtained in this work is expected not only for optimization of the economic benefit, but also for identification of malfunctions of the column, debottlenecking a process, solving process troubleshootings and training the operating staff. Moreover, it can lead to future studies in broader scopes such as simulation all unit processes in this case study or in other refinery plants.

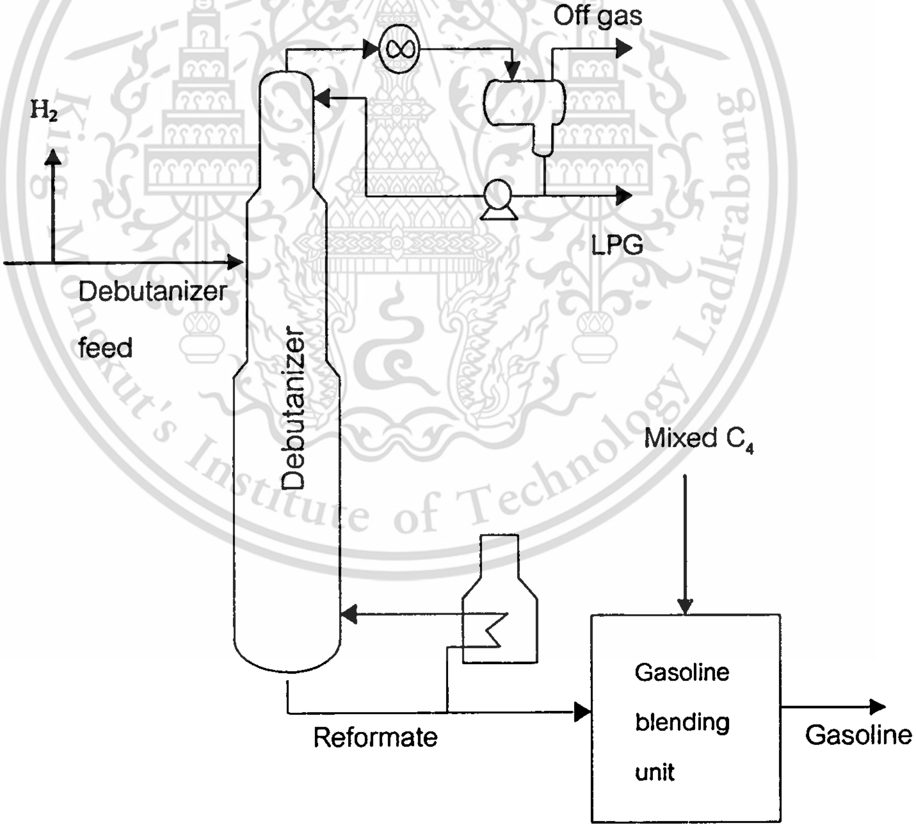


Figure 1.1 A simplified flow diagram of the debutanizer in the platforming unit

1.2 Objectives

1.2.1 Obtain the simulation model which represents the actual characteristics of the existing debutanizer.

1.2.2 Determine the optimal operating conditions for the existing debutanizer to achieve the maximum economic benefit, which is focused on LPG and/or reformate with respect to debutanizer column pressure and reboiler heat duty.

1.3 Hypothesis

Although the debutanizer is operated smoothly, it may not achieve the highest economic benefit. Simulation model and results lead to the improvement of plant performance - plant operation benefits arise for higher yields of valuable products, less giveaway and energy consumption.

1.4 Scopes of this study

1.4.1 Study process background and review the literatures involved.

1.4.2 Create the simulation models for the existing debutanizer.

1.4.3 Propose the best simulation results as the guidelines for the optimum operating conditions of the existing debutanizer for the maximum economic benefit.

1.5 Outcomes

1.5.1 Production guidelines to maximize the economic benefit.

1.5.2 Efficient use of resources and cost down for process adjustment regarding the existing debutanizer.

1.5.3 The developed simulation model is possibly applied to future works such as process limitation, debottlenecking a process and solving process troubleshootings.

Chapter 2

Theory

2.1 Refinery background [1, 3-5]

Refinery process separates crude oil, which is a liquid mixture mainly hydrocarbons, to many products used as fuels or petrochemical feedstocks such as refinery gases, liquefied petroleum gas, naphtha, kerosene, gas oil, lubricating oil, heavy fuel oil and asphalt. Most refinery processes can be grouped into one of three classes as follows [3]:

1. Separation, usually distillation, gives the desired types of compounds,
2. Conversion, usually cracking, changes molecular weight and boiling point,
3. Upgrading, e.g., hydrotreating, meets product-quality specifications.

An overall flow diagram of refinery processing steps is shown in Figure 2.1. Crude oil is fed into distillation units to separate into semiproducts. Light and middle semiproducts are generally fed to upgrading units (e.g., hydrotreating, alkylation, isomerization and platforming unit) to improve product quality. Heavy semiproducts are often fed to conversion units (e.g., hydrocracking, steam cracking, catalytic cracking, coking and visbreaking) to increase yield of middle products and produce light products. Details of those units have been described in many references.

The case study in this work is the debutanizer of the platforming unit in the north production plant of the Alliance Refining Company Limited (ARC). Crude oil is separated into main semiproducts before feeding into conversion and upgrading units, shown in Figure 2.2. The Alliance Refining Company consists of (1) north production unit (PUN, 155 KSD) and (2) south production unit (PUS, 150 KSD). The PUN refinery configuration has been designed to maximize light and middle distillates which are naphtha, kerosene and gas oil. The processing facilities include crude and vacuum distillations, a NHTU/CCR platforming unit, Diesel/HVGO hydrotreating units, a fluid catalytic cracking unit, LPG and LSR merox units, extraction units, amine treatings, sour water stripping units, sulfur

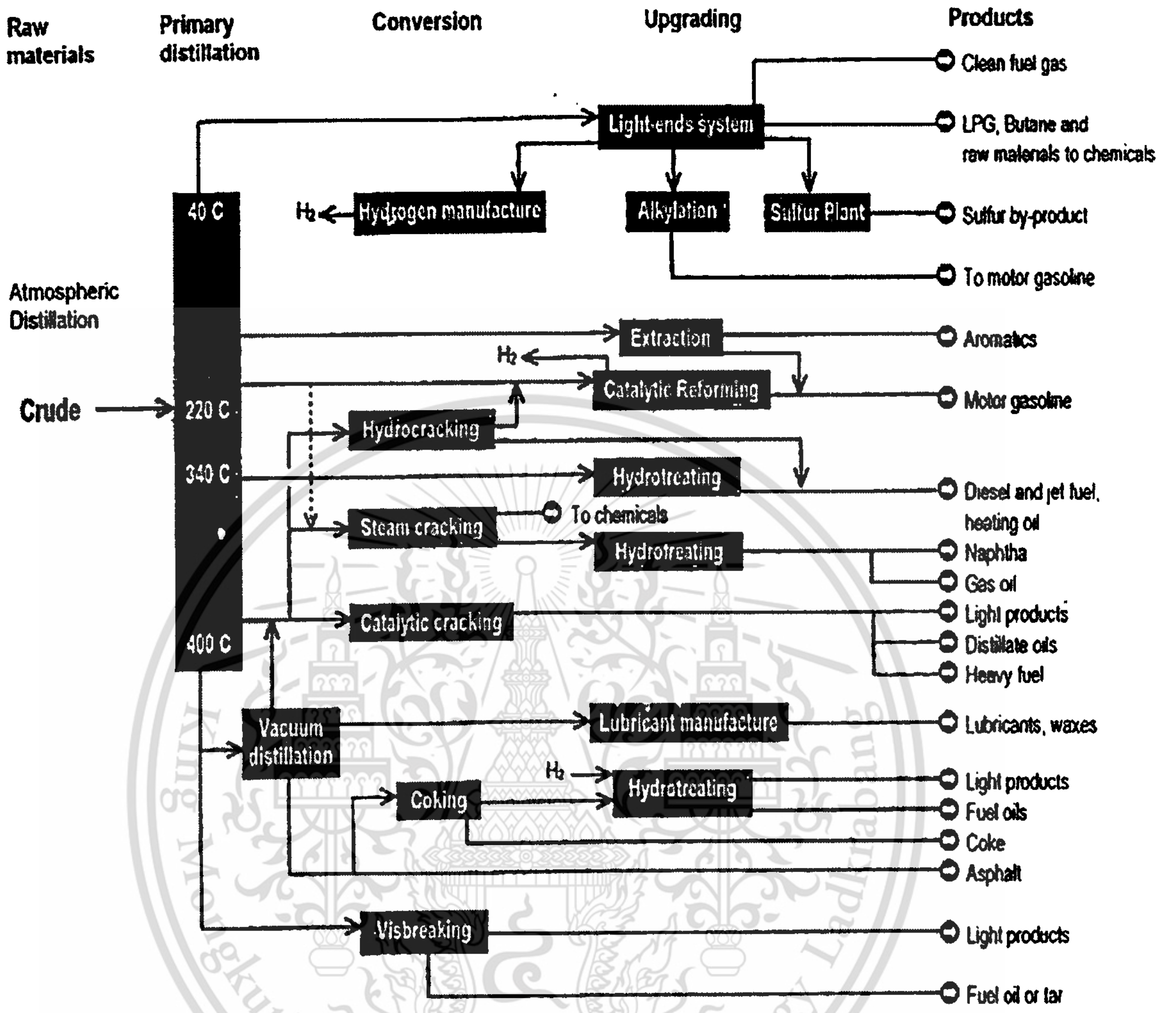


Figure 2.1 A complex petroleum refining process [6]

recovery units with tail gas treating; utilities include a captive power plant; offsite facilities include a wastewater treatment plant and pipelines for crude and products delivery between the refinery and jetty.

Crude oil is pumped to crude and vacuum distillation units as required. The straight run products from the crude distillation unit are sent for further processing in downstream units. Naphtha, from the crude distillation unit, is split into light naphtha and heavy naphtha. Heavy naphtha is processed in the NHTU/CCR platforming unit to produce high octane reformate. This is blended with light naphtha for sale as lead-free motor spirit. The heavy vacuum gas oil (HVGO) produced in the vacuum distillation unit is converted to valuable middle distillates in the fluid catalytic cracking unit. The vacuum residue from the vacuum distillation unit is partly processed to fuel oil and asphalt. The other processing facilities include LPG and LSR merox units and extraction units, which treat straight run LPG, unsaturated LPG, saturated LPG and LSR. All sour fuel gas streams and LPG are treated in amine absorbers to remove H_2S. The rich amine stream is regenerated, and the off gas is sent to the sulfur recovery unit. All sour water streams are treated at sour water stripping units to remove H_2S and ammonia. While the H_2S is sent for sulfur recovery, ammonia is incinerated along with tail gas from the sulfur recovery units. The sulfur recovery unit comprises a Claus section and tail gas treating.

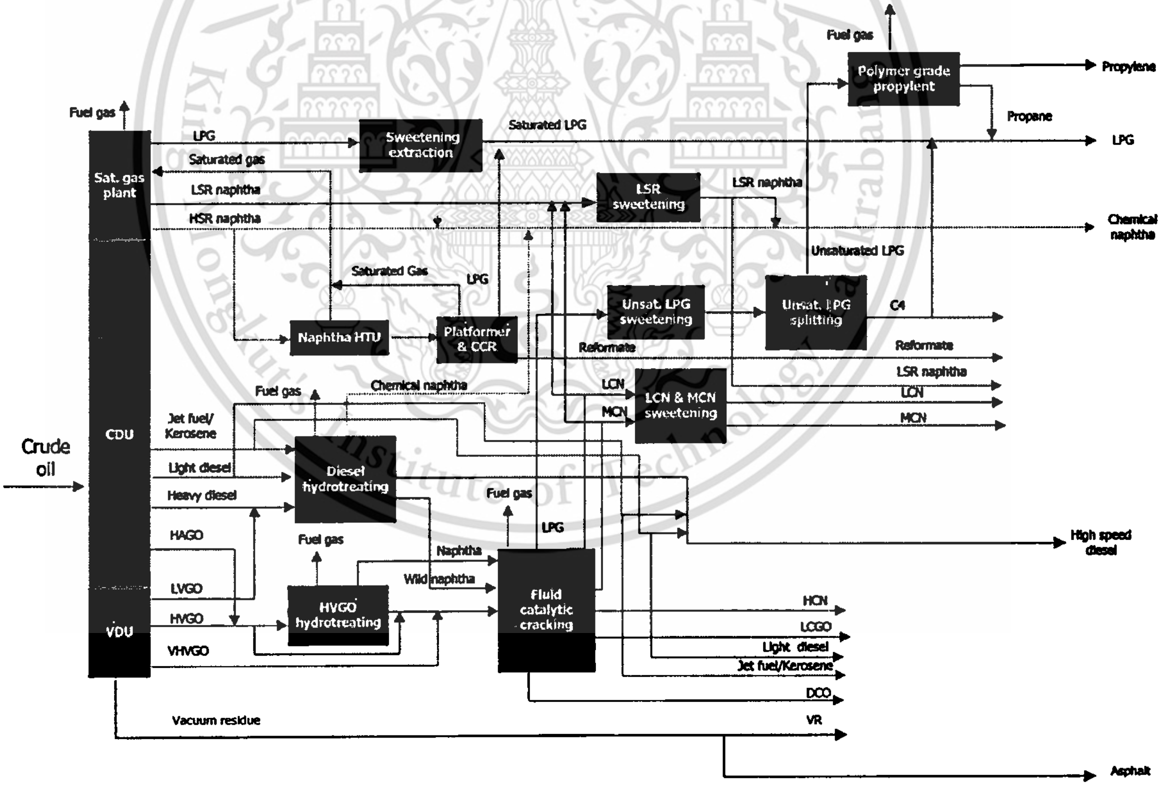


Figure 2.2 Overall processing units of the north production plant of the Alliance Refining Company Limited

2.2 Refinery products [1, 4]

ARC can produce a full-range of refined products that meet the specifications set by Thai Government for domestic consumption, and grades tailored to meet the demand of export customers plus feedstocks for the petrochemical industries. Basically, finished petroleum products are:

2.2.1 Liquefied petroleum gas

A mixture of propane (C_3) and butane (C_4) are known generically as liquefied petroleum gases. The boiling point of propane and butane are -42 °C and 0 °C at normal atmospheric pressure, therefore, they can be kept in the liquid state under only moderate pressures of about 1,400 and 500 kPa, respectively. Propane and butane are recovered from primary crude oil distillation and by cracking of heavy molecules in most upgrading and conversion units. LPG is very flexible in its use, and like natural gas LPG offers the particular advantage of being a clean fuel.

The refinery production of methane and ethane is generally used as refinery fuel in the plant because they would are costly to transport for sale.

2.2.2 Unleaded gasoline (ULG)

Unleaded gasoline is a general term for a light oil cut containing hydrocarbons in the approximate ranges C_5 to C_{11}. Unleaded gasoline or motor gasoline or known as petrol in the UK is a finished product blended in the refinery from a number of components and used as a fuel for a spark ignition internal combustion engines.

2.2.3 Jet fuel / Kerosene

Jet fuel or kerosene is a straight run oil cut, intermediate in boiling range between naphtha and gas oil. It can be used as lighting kerosene which is a domestic heating oil in some countries, including the UK, but its major use today is as jet fuel. Kerosene is the fuel used in jet and turboprop aviation engines. It is also known as aviation turbine kerosene (ATK), Jet A (in USA), Jet A1 (outside USA). Military specifications are also commonplace. Jet A4 is a wide-cut low flash point fuel that, formerly, was widely product for outside USA but its use now largely discontinued. Jet A8 is a narrow-cut high flash point fuel for carrier-based aircrafts.

2.2.4 High speed diesel (HSD)

Automotive gas oil or high speed diesel is a middle distillate oil cut, intermediate between kerosene and heavy gas oil that can be used for diesel engines in commercial vehicles. The important specifications for diesel are cetane index, could point and sulfur content.

2.2.5 Fuel oil (FO)

FO is an industrial fuel, the blending product of vacuum residue or long residue from vacuum distillation unit and other cuts in terms of middle distillates, used particularly in the electricity generation sector. Another application is as fuel for generation of steam for small or medium industries and large marine steam turbines in ocean-going vessels. The two characteristics of fuel oil specifications are viscosity and sulfur content.

2.2.6 Asphalt

Asphalt or bitumen (term used in British English) is a very heavy product, mainly consisting of vacuum residue and heavy vacuum distillates, used in road surfacing and as a waterproofing materials.

2.3 Distillation [7-8]

Distillation is broadly defined as the separation of more volatile materials from less volatile materials by a process of vaporization and condensation. Distillation is based on the difference in composition between a liquid mixture and vapor. The composition difference is due to differing vapor pressures, or volatilities, of the components of the liquid. The most elementary form of the method is simple distillation in which the liquid mixture is brought to boiling and the vapor is separated and condensed to form product; if the process is continuous, it is called flash distillation or an equilibrium flash, and if the feed mixture is available as an isolated batch of material, the process is a form of batch distillation and compositions of the collected vapor residual liquid are thus time dependent.

The term fractional distillation originally was applied to the collection of separations of condensed vapor, each fraction being segregated. Currently, the term is applied to distillation separations in general, where an effort is made to separate an original mixture into several components by means of distillation. When the vapors are enriched by contacting with a continuous feed of liquid mixture and continuous removal of product fractions, the process is continuous distillation, When steam is added to the vapors to reduce the partial pressures of the components to be separated, the term steam distillation is used; if such a process is altered to eliminate the steam, dry distillation (conventional distillation) results.

Most distillations conducted commercially operate continuously, with a more volatile fraction recovered as distillate and a less volatile fraction remaining as residue or bottoms. If a portion of the distillate is condensed and returned to the column to enrich the vapors, the liquid is called reflux. Distillation column normally contains internal devices for vapor-liquid contact; the devices may be trays or packings. It is clear that the difference in volatility of the various components of a liquid mixture is a key to the successful application of distillation. This difference can be related to the thermodynamic equilibrium that can exist between the liquid and vapor mixtures under conditions that can be associated with the distillation. The phase equilibrium relationships are embodied in general area of solution thermodynamics and can be measured or, in a same case, predicted from the properties of pure materials involved. The resulting equilibrium compositions are often referred to as vapor-liquid equilibrium data.

2.3.1 Distillation process [7-8]

Basic distillation involves application of heat to a liquid mixture, vaporization of part of mixture and removal of the heat from the vaporized portion. The resultant condensed liquid, the distillate, is richer in the more volatile components, and the residual unvaporizes bottoms are richer in the less volatile components. Most commercial distillations involve multiple equilibrium stages in order to obtain a greater enrichment than is possible by a single vaporization and condensation. The component separation in simple distillation is limited to the composition deference between liquid and vapor in phase equilibrium; multiple equilibrium stages is used to increase the component separation. Figure 2.3 schematically stacked one upon another. The feed (*F*) enters the column at equilibrium stage (*f*). The heat (q^{-s}) required for vaporization is added at the base of column in a reboiler. The vapors (V^T) from the top of the column flow to a condenser from which heat (q^{-c}) is removed. The liquid condensate from the condenser splits into two streams: a distillate (*D*), which is the overhead product and withdrawn from the system, and a reflux (R) which is returned to the top of column. A bottom stream (*B*) is withdrawn from the reboiler. The overall separation is feed (*F*) separating into a distillate (*D*) and a bottoms (*B*).

Above the feed a typical equilibrium stage is designated as n; the stage above n is n+1 and the stage below n is n-1. The section of column above the feed is called the rectifying and the section below the feed is referred to as the stripping. The mass balance across stage n is: (1) Vapors (V^{n-1}) from the stage below (n-1) flow up to stage n; (2) The liquid (L^{n+1}) from the stage above (n+1) flows down to stage n; (3) on stage (n) the vapors leaving (V^n) are in equilibrium with the liquid leaving (L^n). The vapors moving up the column from equilibrium stage to equilibrium stage are increasingly enriched in the more volatile components. Similarly, the liquid streams moving down the column are increasingly diminished in the more volatile components. The overall column mass balances are:

$$F = D + B \tag{2-1}$$

And for any component i:

$$Fx_i^F = Dx_i^D + Bx_i^B \tag{2-2}$$

A mass balance around plate n and the top of the column gives:

$$V^{n-1} = L^n + D \tag{2-3}$$

And for any component:

$$V^{n-1}y_i^{n-1} = L^n x_i^n + Dx_i^D \tag{2-4}$$

$$y_i^{n-1} = \left(\frac{L^n}{V^{n-1}}\right)x_i^n + \left(\frac{D}{V^{n-1}}\right)x_i^D \tag{2-5}$$

Below the feed, a similar balance around plate m and the bottom of the column is:

$$y_i^{m-1} = \left(\frac{L^m}{V^{m-1}}\right)x_i^m + \left(\frac{B}{V^{m-1}}\right)x_i^B \tag{2-6}$$

Equation (2-5) is the upper (or rectifying) operating line equation and equation (2-6) is the lower (or stripping) operating line equation.

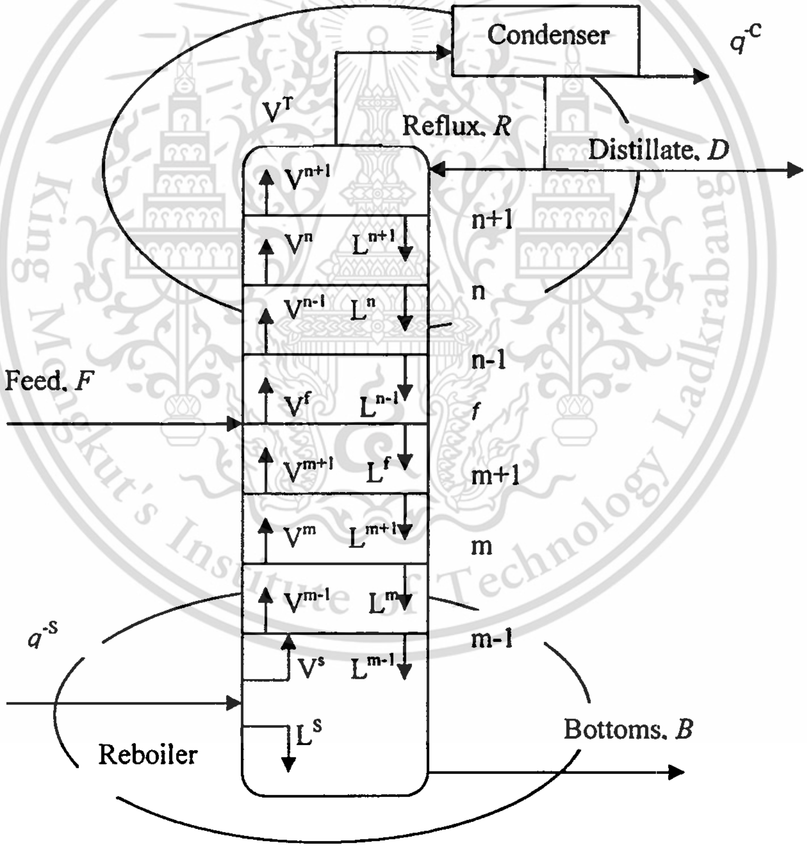


Figure 2.3 Distillation column with stacked multiple equilibrium stages [8]

2.3.2 Reboiler and condenser [1, 8]

Reboiler and condenser are integral part of a distillation system. Reboiler is used to supply heat to a distillation column in addition to that heat supplied by the charge. Liquid is usually withdrawn or pumped from the side or bottom of the column and is reheated by may be a shell and tube exchanger or a fired furnace. Condenser is an equipment that provides condensation through the use of a coolant, usually a cooling water heat exchanger or an air fan cooler. Condensation is the process of converting vapor into liquid by extracting heat. The liquid is called condensate.

In a total condenser the entire overhead vapor is condensed to the liquid state. When the heat load or duty on the condenser is exactly equal to the latent heat of the saturated liquid from the distillation column, the condensed liquid will be a saturated bubble point liquid. The condenser and accumulator pressure will be the total vapor pressure of the condensate. The condensed stream is split into one going back into the column as reflux and the remaining portion leaving the system as distillate product. Partial condenser represents by the relations for the rectifying and stripping sections. The key point to note is that the product is a vapor, which is in equilibrium with the reflux to the column top tray, and hence the partial condenser is actually serving as an "external" tray for the system and should be considered as the top tray when using the equations for total reflux conditions. In the partial condenser all condensate liquid is returned to column as reflux, while vapor is withdrawn from the accumulator as product.

2.4 Platforming unit (Catalytic reforming) [1]

Platforming unit or catalytic reforming is a major petroleum refining process and owes its growth to the ever-increasing demand for high-octane gasoline, major automotive fuel, aromatics and important building blocks of the petrochemical industry. The main objective of this process is to upgrade low-octane naphtha to high-octane reformate for use as high-performance gasoline fuel. The process may be alternatively operated to produce high yields of aromatics for petrochemical feedstocks. At present, several processes are being used in the refining industry; the main differences between these processes are

(1) nature of catalysts, (2) the catalyst regeneration procedures, and (3) the conformation of equipment.

The first process of platforming unit used platinum-on-alumina catalysts which were developed by UOP in the late 1949s to produce large quantities of high-octane reformate and high purity hydrogen. The process has been adapted to bimetallic catalyst and to continuous catalyst regeneration. The platforming process is one in which light petroleum distillate or naphtha is contacted with a platinum-containing catalyst at elevated temperatures and hydrogen pressure normally ranging from 100 to 500 psig (700 to 3,500 kPa). Products obtained from platforming include a high-octane liquid product that is rich in aromatic compounds. Chemical hydrogen, light gas, and liquefied petroleum gas reaction by-products are also produced.

A simplified platforming unit flow diagram of the ARC is presented in Figure 2.4.

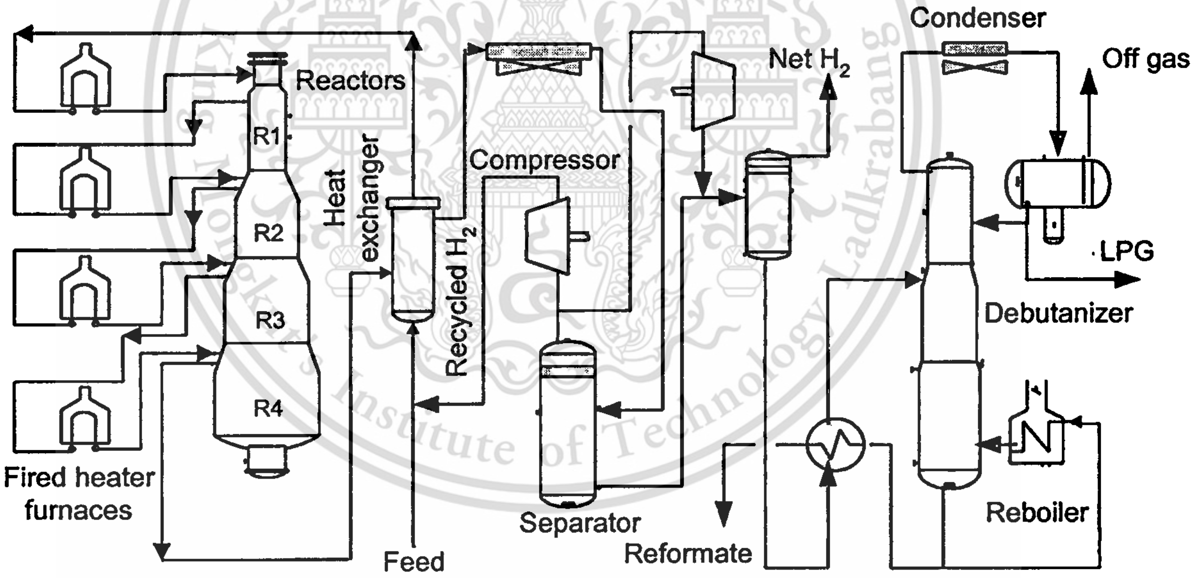


Figure 2.4 A simplified flow diagram of the platforming unit [1]

In the process flow, feed to the platformer is combined with recycled hydrogen, raised to the reaction temperature by a heat exchange and fired heater furnaces and charged to the reactor section. Because most of the reactions, which occur in the platforming process, are endothermic, the reactor section is separated into several stages, or reactors. Inter-heaters are installed between these stages to maintain the desired temperature across all the catalyst in the reactor section. Effluent from the reactors is cooled by the heat exchange with fresh feed and recycled hydrogen in order to obtain the maximum heat recovery. Additional cooling to near-ambient temperature is provided by air cooling. The effluent is then charged to the separation section, where product gas and product liquid separation is ocurred. A portion of gas from the separator is recycled to the reactors with a compressor, while the net gas hydrogen production is sent to hydrogen users or used as fuel. The separator liquid is pumped to a product debutanizer. This debutanizer is a fractionator in which more volatile, light hydrocarbons are removed from the high-octane refromate.

2.4.1 Debutanizer [1]

A debutanizer is one of the separation columns in platforming unit. In this unit, the LPG and off gas are separated from reformate. Debutanizer employs a reboiler (a fired heater) at the bottom of the column to generate its own stripping vapor, which strip the constituents from the bottom product, and employs a condenser at the top of the column to provide reflux, which removes the constituents from overhead products. In the column, the vapor rises through the column, contacting the down flowing reflux stream, as a result, the lighter components concentrate at the top of the column and the heavier components concentrate at the bottom.

The feed liquid stream from reactor product separator is heated from about 42°C to about 181°C before being fed to tray number ten of the debutanizer. The debutanizer is a distillation with thirty sieve trays, condenser and reboiler; the bottom trays (one through ten) are two-pass trays and the top trays (eleven through thirty) are single-pass trays. The debutanizer overhead vapor stream is routed to the tube side of the overhead condenser, air-cooled exchangers. The overhead vapor stream is cooled from about 72°C to about 43°C in passing through the condenser. The mixed phase debutanizer overhead stream flows to reflux drum where it is separated into a vapor stream (off gas) which flows to the saturated gas plant, and the liquid stream (LPG) which is pumped as a reflux to the twenty-second tray and storage tanks. The debutanizer bottom streams are routed to the reboiler and exchangers for run down reformate.

The reboiler is a fuel gas fired heater, which vaporizes about half of the circulated debutanizer bottom stream to provide heat input to the debutanizer. The remainder of the bottom stream (reformate) is cooled in the bottom exchangers. The reformate stream is cooled from about 244°C to about 43°C and then flows to storage tanks.

2.4.2 Debutanizer column control [1]

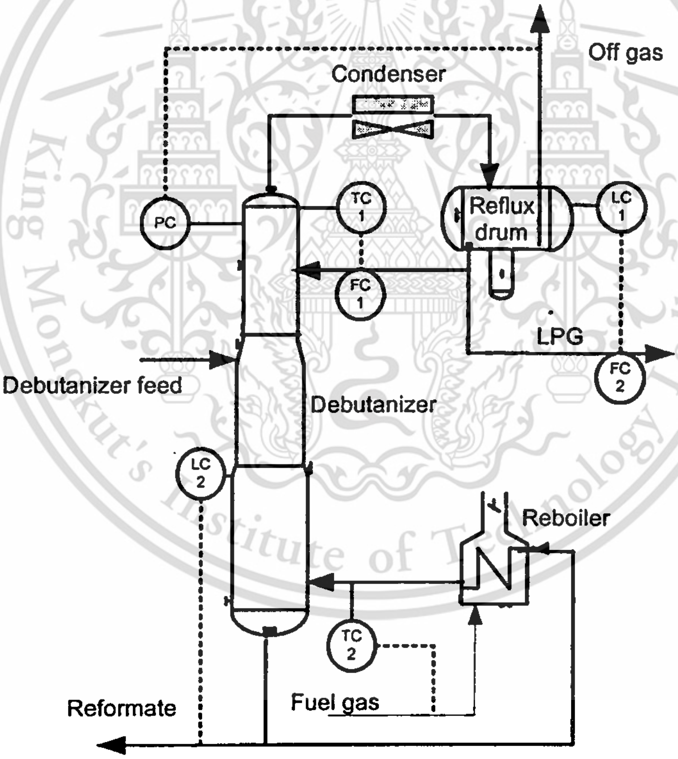


Figure 2.5 Common debutanizer control scheme [1]

Column pressure is perhaps the most important control variable in a distillation column. Pressure affects condensation, vaporization, temperatures, compositions, and almost any process that occurs in the column. A debutanizer column will not achieve stable operation unless steady pressure can be sustained. Debutanizer column pressure has to be normally controlled by venting a vapor product stream via pressure controller (PC) to flare or saturated gas plant.

Column temperature is perhaps the most popular means of controlling product composition. The control temperature is used as a substitute to product composition analysis. A change in control temperature represents a corresponding variation in the concentrations of key components in the product. The liquid stream in reflux drum is pumped to two locations. The reflux flows to the second tray in the debutanizer through a flow controller (FC1), which is set by the temperature on tray number twenty-two of the debutanizer column (TC1). The on-spec LPG flows to LPG storage tanks through a flow controller (FC2), which is set by the reflux drum level controller (LC1). The debutanizer bottom streams are divided in two portions and sent to the following location. The debutanizer reboiler vaporizes bottom stream to provide heat input to the debutanizer. The outlet temperature of the bottoms from reboiler is sent by a temperature controller (TC2), which adjusts the fuel gas flow to the reboiler. The remainder stream (reformate) is cooled in exchangers. The reformate flows through a level controller (LC2) to the storage tanks.

2.5 Optimization and simulation theory [2, 9-11]

Optimization is the process of finding the conditions that give maximum or minimum values of a function. Optimization has always been an expected role of engineers, although sometimes on small projects the cost of engineering time may not justify an optimization effort. A design is often difficult to optimize because of its complexity. In such cases, it may be possible to optimize subsystems and then choose the optimum combination of them. Basic to any optimization process is the decision regarding which criterion is to be optimized. Minimum cost is probably the most common criterion.

Simulation has been defined as the process of developing a computerized model of a system and conducting experiments with this model for the purpose of either understanding the behavior of the system or evaluating strategies for the operation of the system. In the chemical process industries (CPIs), engineers use a process simulator or software package as a tool to deal with a process at all of its life cycle, from synthesis to design, construction, start-up, modification and retirement as shown in Figure 2.6. By performing flowsheeting calculation on a computer, manpower and design costs can be saved. Process modeling reduces the cycle time for new process development by identifying problems and opportunities in the early stages of research, and spot operability problems due to equipment malfunctions and to debottleneck a process. Therefore, simulation is the use of one system to imitate the actions of another for design of new operations, revamps of the existing operations, analysis and improvement of current operation, troubleshooting plant operation and training engineers and operating personnel.

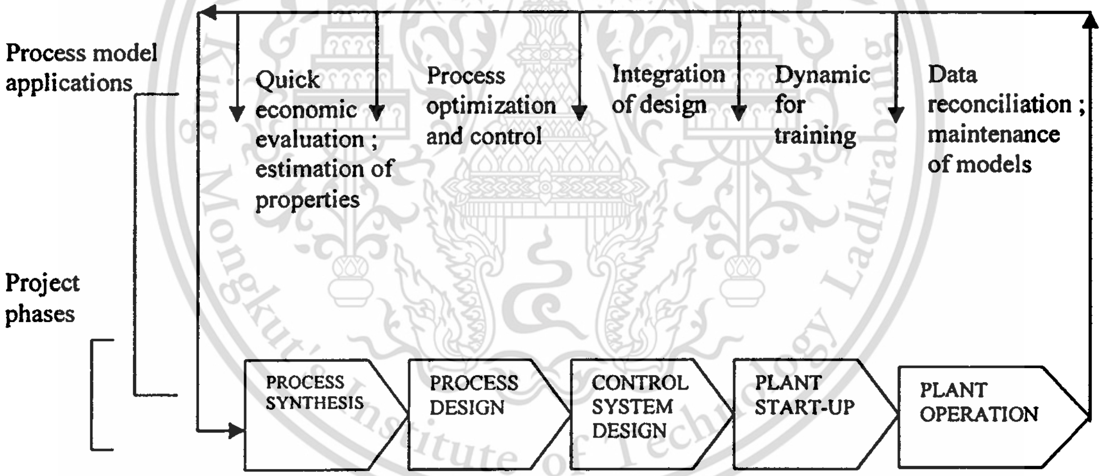


Figure 2.6 Process model applications for chemical processes [9]

The mathematical model, the heart of simulator, divides simulations into two types as dynamic and steady-state simulators. Steady-state simulators-time independence are generally modeled as sets of algebraic equations, so they are easier solved than dynamic simulators. Three approaches employed in the simulators are sequential modular, equation-oriented and simultaneous modular approaches. Sequential modular approach calculates unit operations intact modules as sequentially as the actual process flow. Each module simulates one type of the unit operation, for instance, the heat exchanger module for modeling only heat exchanger, and a large flowsheet could be constructed by combining modules. Figure 2.7 shows simplified structures for sequential modular and equation-oriented simulators. At the top level of the sequential modular approach, the executive program accepts input data, determines the flowsheet topology, derives and controls the calculation sequence for the unit operations in the flowsheet. The executive then passes control to unit operations level for execution of each module. Finally, the executive and unit operations levels make frequent calls to the physical property level for routine tasks such as calculations of enthalpy, phase equilibrium and other stream properties. Although this approach is not suitable for solving the recycle structure of the flowsheet and external design specifications, which create awkward iteration loops in the calculation sequence, it is usually used in the popular current commercial simulators such as PRO/II, which is used in this work, ASPEN PLUS, HYSIM, and DESIGN II.

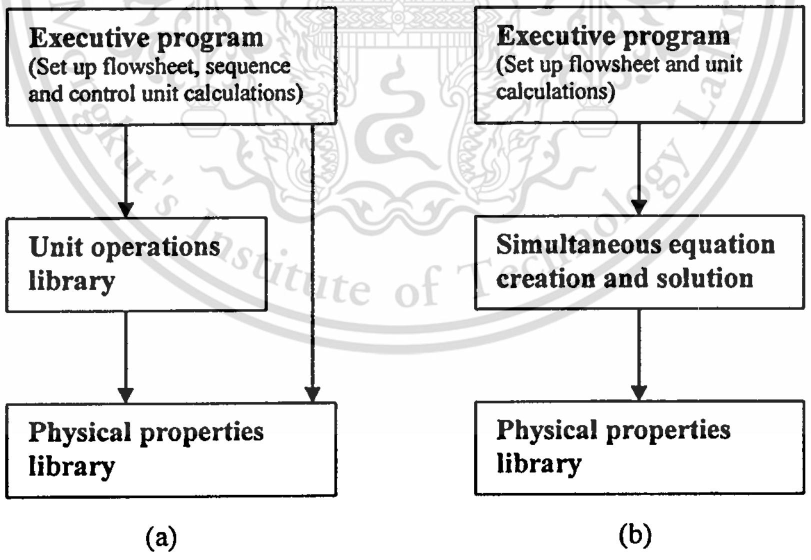


Figure 2.7 Structures of process simulators: (a) sequential modular approach and (b) equation-oriented approach [10]

For equation-oriented approach, process equations are treated by general-purpose solution strategies, e.g., Newton-Raphson, and often solved simultaneously. As seen in Figure 2.7, the executive performs a slightly different function, in that it organizes the equations and controls the general "design" constraints at the flowsheet level, the equation-oriented simulators are much more flexible in terms of solving problems. They also allow the application of much more sophisticated optimization strategies. However, this approach is limited by capabilities of the equation solver. Equation-oriented flowsheeting problems require large-scale numerical algorithm, good initialization strategies and reliable options to prevent convergence failure. This tendency to fail is aggravated by a set of nonlinear physical property equations. To overcome this problem, equation-oriented simulators have been modified to incorporate low-level modules for calculating nonlinear physical properties similar to the sequential modular systems. Examples of equation-oriented simulators are SPEEDUP, ASCEND, and QUASILIN.

Simultaneous modular approach methods are developed from sequential modular approach where unit operation modules, for the most part, remain intact but stream connections are solved simultaneously. In this manner, complicated recycles and flowsheet constraints could be solved together. This development is aids for simultaneous modular methods by application of Broyden-type method, having a much faster convergence rate than sequential modular recycle algorithms. Examples of simultaneous modular simulators include FLOWPACK and MPFPL.

Time-dependence dynamic simulators require an exercise of the system mathematical models as the solutions of sets of differential equations or their equivalents in finite difference equations, matrix equations or statistical expressions. They are suitable to improve safety and control features, debottleneckings and start-up, and train plant operators for emergency response. However, they require more time and higher computer-power than steady-state simulators. The commercial dynamic simulators are, for example, SPEEDUP, which can perform steady-state as well as dynamic simulation, PROTISS, OTISS, and OPTISM.

Simulation is a tool which allows engineers to perform the tasks more effectively, whether designing a new process or analyzing an existing one. The speed of a simulator allows to investigate more alternatives in a given period than if perform the calculations by hand. Furthermore, users can automate flowsheet circulations to avoid repetitive or trial-and-error calculations. For example, simulation model can show plant responses to vary operating conditions or feedstock qualities. This is far more economical than running costly plant tests. Since simulators always access their own standardized databases, once simulation models are valid, any engineer can use it to produce consistent and accurate results.

The chemical process and design industries use simulators for:

- Designing new operations
- Retrofitting the existing operations
- Troubleshooting plant operations
- Optimizing the existing operations

When designing new operations, more cases can be analyzed using a simulator so as a better design can be generated. When retrofitting an existing operation, a simulator can predict how the plant would respond if the feed rates were changed or if an existing piece of equipment was used in a different service. As a troubleshooting tool, simulators help identify bottlenecks and perform energy conservation studies. With the aid of a simulator, the processes can be optimized to increase profit and/or lower operating costs. In the computer simulation of any physical process, it is important to distinguish between accuracy and precision. Accuracy is a measure of how well the simulation results match reality. Precision is a measure of how well the simulator solves the equations that describe the process. Simulators can deliver the precision but not necessarily the accuracy.

2.5.1 Simulating reality [11]

Although simulators may not deliver or guarantee the required accuracy, proper understanding and selecting of the appropriate thermodynamic method attain the accuracy of the simulation results. The cubic equations of state (EOS) does not only calculate phase equilibrium but also all the necessary thermodynamic properties for a comprehensive model of an entire flowsheet. Cubic EOS based on the Van der Waals EOS was initially too simple to provide results sufficiently accurate for engineering calculations. Van der Waals theory basically states that all fluids at the same reduced coordinates have the same physical temperature and pressure, and, therefore, the original Van der Waals EOS is a two-parameter corresponding stage model.

Redlich and Kwong made some progresses on the issue, with a carefully crafted cubic EOS to provide better physical properties than the original Van der Waals formulation, still using two parameters, i.e., critical temperature and pressure. However, it was not enough for engineering calculations since it was not accurate enough for the prediction of properties of compressed gases and liquids, as shown in Figure 2.8. Later, Wilson made a simple modification of the attractive term of the Van der Waals EOS for the prediction of the physical properties of gases such as ammonia. Unfortunately, Wilson's approach did not give accurate vapor pressure around the normal boiling point and so was not popular. Nevertheless, Wilson's suggestion about using the acentric factor as a third parameter for an EOS did not go unnoticed.

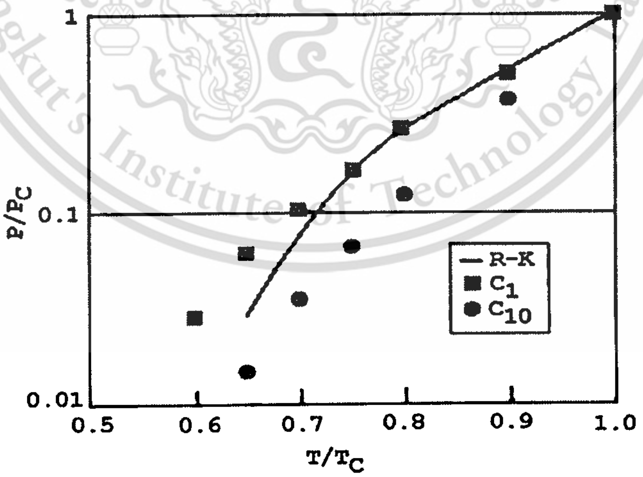


Figure 2.8 Redich-Kwong reduced vapor pressure and data for C$_1$ and C$_{10}$ [11]

In 1972, Soave created a clever parameterization using the acentric factor as a third parameter for cubic EOS that was accurate enough for general natural processing calculations. It was quickly extended to refinery application. Soave's model was also simple enough to be useful with very few physical properties as input, basically the critical pressure, temperature and vapor pressure. Other EOS quickly followed such as the Peng-Robinson. Some enhancements were tried via additional correlating parameters, like dipole moments and radius of gyration, thus, creating four-parameter EOS, but only offered minor enhancements when compared with simpler EOS, while requiring more data.

The relative paucity of required experimental information by cubic EOS, combined with the ease of solution and the ability of estimating enthalpies and entropies in the shape cast by Soave intersected in an interesting way with the birth of microcomputers and the desire to do process simulation calculations inexpensively. With the introduction of Russell's inside-out method for distillation calculations, microcomputers of the mid-1980s were powerful enough to calculate flowsheets for the oil refining industry, including crude towers. This resulted in a revolution in process calculation, as discussed by Svrcek which involved the physical property data. Table 2.1 shows the lineage of commonly used cubic EOS. Table 2.1 does not even begin to cover the variety one found in the literature related to cubic EOS [12-14]. At any rate, it seems as if almost everything could be accomplished without going through the tortuous path of activity coefficients and standard states. Successful EOS such as Soave's can be thought of as generalized vapor-pressure equations, which are, in turn, functions of the pure-component critical pressure, temperature, and acentric factor

Since the saturation pressure of nearly immiscible systems such as water/hydrocarbon is close to the sum of the water and hydrocarbon vapor pressure, simple cubics can be used for many natural gas and refinery problems. Thus, if the vapor pressure is calculated by one accurately for polar and nonpolar compounds, the calculating complex vapor-liquid equilibrium (VLE) can be hoped if a sufficiently flexible mixing rule for the EOS is available. EOS is a compact model that can predict thermal properties without any supplementary data except, of course, ideal heat capacity. They are consistent in that they provide a smooth transition between the liquid and vapor phase, allowing the modeling of processes near the critical point.

Table 2.1 Common cubic equations of state [11]

Equations of state	Repulsive part	Attractive part	Engineering	Mixing rules
Van der Waals	$\frac{RT}{V-b}$	$-\frac{a}{V^2}$	A scientist's scientist EOS. Physics are simple, but we sick to the assumptions and consequences.	$b=\sum x_i b_i$ $a=\sum\sum\sqrt{a_i a_j x_i x_j}$
Redich-Kwong	$\frac{RT}{V-b}$	$-\frac{a}{V(V+b)\sqrt{T}}$	Inspired but empirical modification. "*a*" term dependent on *T*.	
Soave-Redich-Kwong	$\frac{RT}{V-b}$	$-\frac{a(T)}{V(V+b)}$	Clever parameterization using A = f(T, ω); k_{ij} can be generalized HC*/HC pairs, water/HC, light gases and HC. Ch.e.. at necessary for polar substances.	$b=\sum x_i b_i$ $a=\sum\sum(1-k_{ij})\sqrt{a_{ii}a_j x_i x_j}$
"Chemical" SRK	$\frac{RT}{V-b}$	$-\frac{a(T)}{V(V+b)}$	Sledgehammer parameterization using $a=f(T_r,\bar{c})$ where the last term is a vapor of parameters going (usually) from 1-5, unique for each substance. Flexible mixing rule based on activity coefficient models	$b=\sum x_i b_i$ $a=b\left[\sum x_i\left(\frac{a_i}{b_i}\right)+\frac{G^E}{\sigma}\right]$

* HC = Hydrocarbons

Consider Table 2.2, and will see that things are not that different. Note that the pressure is assumed sufficiently low to discard nonideality effects to the gas-phase fugacity coefficient, if not a model is assumed for the vapor phase. The table is very general, and with exceptions it can always be found where these general observations will fail. Nevertheless, there is a trend. As the problems to solve become more involved, the models, either activity coefficient or EOS based, tend to be more complex, requiring more physical properties either pure component or mixture, and are less predictive in nature. This is the essence of when using any of thermodynamic model in process simulators. In general, they are based on relatively simple theories that have to be tweaked to work under industrial situations. These tweaks are implementation-dependent and sometimes poorly documented. Predictions depend upon the model chosen, and its applicability is system-dependent. Generally, the more polar the system, the more experimental data will be needed for a reliable prediction, and these will be of less value.

Table 2.2 Equivalencies between simple EOS and activity-coefficient-based models [11]

Problem type	EOS	Similar activity coefficient	Physical properties
Petroleum refinery	SRK, PR Special handling for water.	Generalized vapor pressure equation (e.g., Lee-Kesler). Ideal solution or regular solution.	Critical pressure, critical temperature, and acentric factor. Special parameters for water (pure-component and mixtures).
Petrochemicals	SRK, PR Special handling for water and other polar compounds.	Generalized vapor pressure (e.g., Lee-Kesler) regular solution, one-parameter activity-coefficient models.	Critical pressure, critical temperature, and acentric factor. Special parameters for water (pure-component and mixtures).
Chemicals	Modifications of SRK and PR as suggested by the "chemical" SRK.	Antoine equations plus 2-3 parameter activity-coefficient models.	Empirical attractive-term equation plus 2-3 parameters for Gibbs excess (activity-coefficient) model.

A, perhaps, not immediately evident weakness of more complex cubic EOS lies in their very strength. Because they are intrinsically consistent models, their predictions of varied sets of properties are intimately connected with the fundamental laws of thermodynamics. This is good in general, but it can hinder the model in such a way that it is not useful. For example, excess enthalpies will be automatically predicted when an EOS is used. These enthalpies will be found as a by-product of the VLE modeling done to determine the parameters. In turn, these enthalpies may or may not be accurate. Traditional activity coefficient models have limitations on the magnitude of the excess enthalpies they can predict. How these models behave inside cubic EOS for the calculation of derived properties is not well known, and is disappointing sometimes. So, if a system is modeled with significant excess enthalpies using a Gibbs free-energy-based EOS and a good VLE is fit, this does not automatically ensure user a good overall model from energy balance point of view.

2.5.2 Tips of simulations [11, 15]

Process simulations are widely used to obtain a better understanding of a particular process. These simulations are used to answer questions such as how can yields be improved, or how should the available independent variables be set to maximize profit. Although current process simulations are greatly improved, there are many reasons why a process simulation doesn't match the plant. Understanding these reasons can assist in using simulations to maximum advantage.

One category is the simulation effects which include using theoretical equilibrium separation stages in a distillation model but having actual trays with imperfect separation in the tower. Thermodynamic calculations always have error, the large number of components in refineries leads to estimate. Interactions between components may not be accounted for. A variety of thermodynamic packages are available and proper selection can be critical to achieving valid results. Stead-state processing is assumed in most process simulators, yet the actual plant is rarely or never at steady state since the most modern refineries have so many minor and major process changes. However, this error may be small. Simulations can be useful tools for understanding and improving process operations when properly applied. Simulation results should be always treated with caution and a degree of suspicion. There is no substitute for experience in choosing, setting up and implementing a simulation. For most chemical process simulations, vapor pressure is one of the most important properties. Make sure it is as good as needed for the desired accuracy of model and understand what the simulator has estimated and how. Pure component and mixture have to be checked. If any calculations related to energy balances are performed, the mixture enthalpies and heat capacities should be checked. Transport properties should be checked, if going to design exchangers. There is much less work on those properties than on VLE. In case of designing trays, pressure is important and surface tension plays a key role in a pressure drop caculations.

2.5.3 Optimization [2, 15]

Optimization is one of major quantitative tools in the machinery of decision making. A wide variety of problems in operation of chemical plants can be resolved by optimization. The goal of optimization is to find the values of the variables in the process that yield the best value of the performance criterion. Typical problems in plant operation have many and possibly infinite number of solutions. Optimization is concerned with selecting the best among the entire sets by efficient quantitative methods. Computers and associated software make the computations involved in the selection feasible and cost effective. But to employ computers and software require (1) critical analysis of the process or design (2) insight about what the appropriate performance objectives are (What is to be accomplished), and (3) use of past experiences or engineering judgement.

In plant operation benefits (the largest production, the greatest profit, the minimum cost, the least energy use and so on) arise from enhancements in the operation of the equipment or improving plant performance, such as improving yields of valuable products or decreasing yields of contaminants and energy consumption, and improving higher processing rates and longer times between shutdowns. However, prediction of benefit must be done with care. Operating variables in most plants are always coupled in some way. A few percentage savings may justify an energy conservation project. In a unit operation such as distillation, it is incorrect to simply sum up the exchanger duties and claim percentage reduction in total heat required. A reduction in the reboiler heat duty may influence both the product purity and quantity, which can translate to a change in profits.

In optimizations, economics usually drive the simulation. Mistakes in assigning values to streams, qualities and energy can lead to errors. In the refinery process, the values of many intermediate streams are usually not known since they are neither purchased nor sold. Such stream values must be calculated. There are many procedures to calculate intermediate stream values. Economic errors can completely invalidate an otherwise acceptable simulation system that has the proper model. For this reason, some operators choose not to use economic values in their optimizations and concentrate instead on maximizing some other parameters such as yield of a desired product. Additional optimization errors can occur when selecting constraints and manipulated variables. The use of the wrong constraints, or incorrect values for the proper constraints can lead to optimization errors. Selecting the proper manipulated variables is also crucial.

Optimal operation of stage distillation column; As distillation is probably the most widely used separation process in industry, objective functions such as maximize separation, maximize productivity of top and bottoms and minimize energy consumption are the optimization technique that needs to be applied to steady-state wise distillation.

2.6 Commercial simulation softwares [16-17]

Chemical engineers use process simulation to perform a variety of important works. Generally, the successful work ranges from calculations of mass and energy balances of large flowsheets to predict of the performance of process alternatives that can save millions of dollars. An engineer very quickly can define a complex flowsheet and all the process conditions. Desktop computers now allow rating, sizing, optimization, and dynamic calculations that previously required large mainframe computers. In the past, the simulations were often built by a group of experts, including a physical property expert. Now, simulators such as ASPEN PLUS, ChemCAD III, HYSIM, PRO/II, and SPEEDUP are easier to use and more powerful than the stand-alone programs of the past.

2.6.1 PRO/II [16-17]

PRO/II is SIMSCI's latest flowsheet simulator, a product of four generations of the development. Like its predecessors, PRO/II was upgraded the calculation engine and gave a partner called PROvision. PROvision is a super-responsive interface that gives PRO/II the flexibility of a true Window^{TM} environment. Together, PRO/II and PROvision help users solve the widest range of industry applications with the greatest ease.

SIMSCI designed its first flowsheet process simulator, SSI/100, after the distillation program SP05. SSI/100 had breakthrough capabilities for its time in 1974. In 1978, SIMSCI created the process simulation program. It expanded the component and thermodynamic databases. It added more unit operation calculations as well as flowsheet tools, like an optimizer and a calculator, which has in-line FORTRAN capabilities. This program made flowsheet simulator accessible, since it ran on nearly every mainframe and personal computer.

PRO/II is a comprehensive computer simulator that models steady-state processes found in the chemical, petroleum, natural gas, and synthetic fuels industries. It operates in a sequential modular fashion; each unit is calculated separately with the calculations proceeding in a stepwise fashion from one unit to another. PRO/II combines the data resources of a large chemical component library and extensive thermodynamic properties prediction methods, with the most advanced and flexible unit operation techniques to provide the process engineer with the computational facilities to perform all necessary mass and energy balance calculations to model most steady-state processes.

2.6.2 The main components of a PRO/II simulation [16]

Because PRO/II is a modular simulator, the input data are entered in almost any order when using a simulator. Keyword input, however, must be ordered very specifically. In either mode of input, all required data must be provided correctly to successfully run a simulation. Figure 2.9 illustrates how information linked in PRO/II simulation and how the various input data categories impact one another.

Accuracy is largely determined by a few key judgements that the user must make. The accuracy of the simulation results primarily concerns the selection of the thermodynamic method. The thermodynamic models can be a large source of error in process simulation. This is particularly true when the user is careless in selecting a method. Since it is not possible to develop a single thermodynamic method to model all chemicals under all conditions, PRO/II uses several different models, for example, SRK, PR, etc. Each

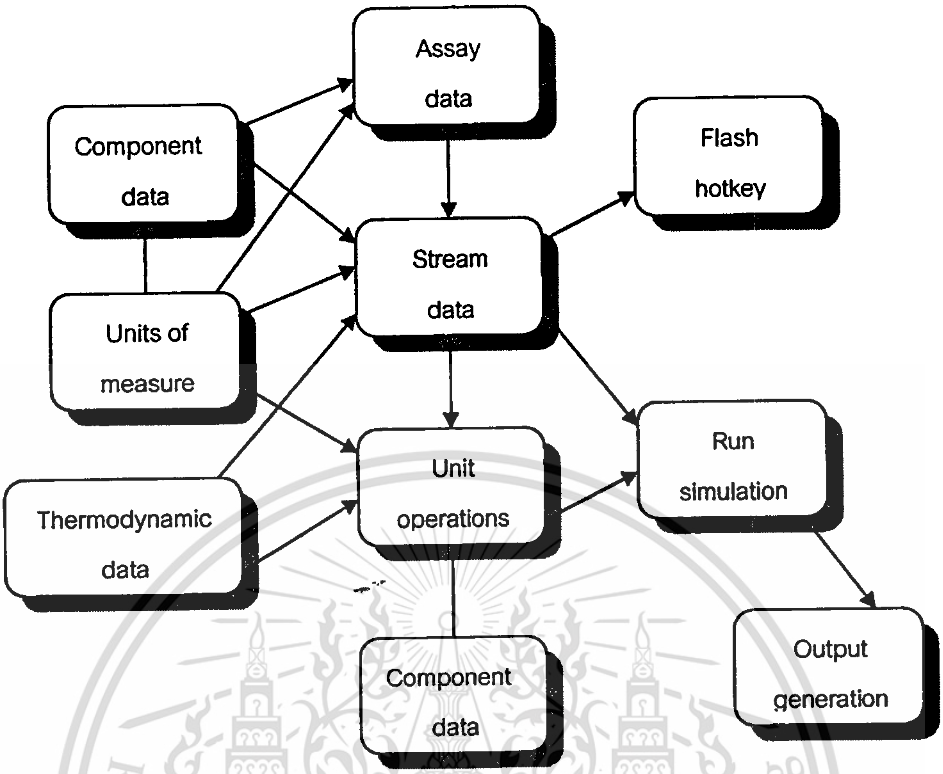


Figure 2.9 Components and information flow scheme in PRO/II [16]

model works well in some situations and poorly in others. The selected appropriate methods are applied for particular flowsheet. Polar components at high pressure should not be simulated with a thermodynamic method that was designed to model low-pressure hydrocarbons. The experience and engineering judgement should be applied to check that the results are reasonable. The selection of thermodynamic methods has to be considered to be one of the most crucial decisions when developing a simulation. Generally, the thermodynamic property methods must be selected for:

- Equilibrium K-values
- Enthalpies
- Entropies
- Densities.

The thermodynamic methods available in PRO/II may be classified into six categories:

- Ideal methods
- Generalized correlations
- Equations of state
- Liquid activity methods (LACT)
- Special packages
- Electrolytes.

Ideal methods

Ideal methods (sometimes referred to as "pure method") calculate the mixture properties as weighted sums of the pure component properties. Each component's contribution is proportional to its quantity in the mixture. While ideal methods often provide good approximations for enthalpies and densities, more sophisticated methods are almost always required for K-values.

Generalized correlations

Generalized correlations are empirical or semi-empirical methods, mostly based on the principle of corresponding states. They generally do not contain any adjustable binary parameters and are primarily useful for nonpolar hydrocarbon mixtures. Examples of generalized correlations include the Braun K-10 (BK-10), Grayson-Streed (GS) and Improved Grayson-Streed (IGS) methods.

Equations of state

Equations of state used in this work are mathematical expressions which involve the density, temperature, pressure and composition of a fluid. From an equation of state, the component K-values as well as the enthalpy and entropy which deviate from their ideal gas value can be calculated. Well-known examples of equations of state are the ideal gas law and the Van der Waals equation. More modern equations of state include the Soave-Redlich-Kwong and Peng-Robinson equations. These equations generally involve the use of binary interaction parameters denoted by K_{ij}, to account for interactions between different components. The basic SRK and PR equations are useful for systems of nonpolar hydrocarbons; more sophisticated modifications are available to better represent systems containing polar components and to calculate rigorous vapor-liquid-liquid equilibrium.

Liquid activity (LACT) methods

LACT methods calculate K-values by starting with an ideal solution and correcting the result with activity coefficients. The activity coefficients are calculated from a model for the excess Gibbs free energy of the liquid mixture. The most commonly used methods are Non-random two-liquid equation (NRTL) and the Universal Quasi-chemical (UNIQUAC). The binary interaction parameters are usually necessary. Dissolved gases may be modeled with Henry's Law, and a heat of mixing option may be used to correct for nonideality in the liquid enthalpy. If the necessary parameters are available, LACT methods can successfully describe a wide variety of nonideal mixtures (particularly mixtures of components having similar volatility) including mixtures exhibiting two liquid phases.

Special packages

PRO/II contains several special packages designed for thermodynamic calculations on the specific systems. For example, glycol package with modified-SRK, sour package, amine package, alcohol package, etc.

Electrolytes

PRO/II is available for system in which aqueous electrolyte chemistry is important.

Table 2.3 shows some applications for the most common forms of thermodynamic methods. The accuracy of the simulation hinges largely on the selection of the correct thermodynamic method that brings the reasonable results. Additionally, transport properties like viscosity, thermal conductivity, vapor-liquid surface tension, and liquid diffusivity are also available and specified in the thermodynamic data. The computing transport properties are available and can be calculated by pure, petroleum and Trapp methods. The petroleum method uses predictive correlations, including pressure correlations, that apply to bulk hydrocarbon mixtures.

Table 2.3 Thermodynamic methods and application examples [16]

Form	Application	Examples of thermodynamic method
Generalized correlation	Low pressure crude systems involving heavy hydrocarbons: vacuum and atmospheric crude towers	BK-10, GS, IGS
Equations of state	Light hydrocarbon systems, hydrogen-rich systems: reformers and hydrotreaters	SRK, PR
Liquid activity method	Non-ideal chemical system: Aromatic/non-aromatic extraction, chemical systems with small amounts of supercritical gases	NRTL, UNIQUAC, NRTL with Henry's Law

In the petroleum refining industry, feedstocks contain thousands of components and, consequently, are characterized in terms of assays rather than detailed component breakdowns. PRO/II provides the great flexibility when entering assay data and performing simulations with assay-characterized feedstocks. There is no need to correct for pressure or translate the American Society for Testing and Materials, distillation 86 (ASTM D86) data to true boiling point (TBP) data because PRO/II will perform all assay processing.

Chapter 3

Literature Reviews

Process simulations or mathematical models are widely used by plant engineers and planners to obtain a better understanding of a particular process. The simulations, for example, are used to find the answers of how can feed rate be increased, how can yields be improved, how can energy consumption be decreased, or how should the available independent variables be set to maximize profit? Understanding these reasons can assist in using simulations to maximize advantage. The researches involved are reviewed as follows.

Kister et al. [18] described a case where a seemingly minor mismatch led to the discovery of a major simulation deficiency. Undiscovered, the deficiency would have led to a failed tower debottleneck. The match between field data and simulation can make or break the outcome and success of column troubleshooting. This paper expanded and focused on column troubleshooting. A simulation that did not reflect the real world steered a troubleshooting investigation toward an incorrect diagnosis and into inadequate solution. Once revised to reflect the real world, the same simulation proved invaluable for identifying the correct root cause and guiding the investigation toward the proper solution.

The column is in Copene's aromatic plant in Camacari, Bahia, Brazil. It performs a sharp split between two close-boiling isomers, A1 and A2, which constitute most of the distillate, and a heavy boiler, B, which constitutes most of the bottom product. A preliminary tower simulation was available prior to the task force formation. A good simulation must use a correct vapor-liquid equilibrium data. For the A/B separation, which is a relatively easy hydrocarbon separation, relative volatility of about two, there has been good experience using a cubic equation of state such as the Soave-Redlich-Kwong (SRK) or Peng-Robinson (PR). A number of checks indicated that both the SRK and PR equations gave similar results for this simulation

Klaithong [19] studied a dynamic distillation calculation using thermodynamic models of which SRK equations of state had been reported to be highly successful. This work demonstrated without doubt the effectiveness and usefulness of phase equilibrium predictive methods base on the molecular interaction forces between the mixture components when they were applied to an actual distillation column, the debutanizer column of the Bangchak Petroleum Public Company Limited. The design method adopted in this work was divided into 2 stages, i.e., generation of thermodynamic calculation and a dynamic distillation. Three thermodynamic models, Generic Redlich-Kwong (GRK), SRK and PR, were used in calculation. The starting point of the generation of thermodynamic equilibrium stage calculations, all thermodynamic properties, i.e., enthalpy, vapor-liquid equilibrium and density of liquid and vapor mixture were calculated by the GRK, SRK and PR models. In the second stage, the dynamic distillation at the debutanizer column was developed. The data was checked for credibility by the existing program, PRO/II. Once the data are accepted as reliable, the actual distillation was applied to study the dynamic behavior.

For different case studies, typical responses of the GRK, SRK and PR models were considered. In every case study, the SRK model showed a reasonably close representation to the actual data of the top and bottom products of the debutanizer column. The PR model was less deviated from the actual data than the GRK model. This work concluded that the SRK and PR models can be applied to the debutanizer column of the Bangchak Petroleum Public Co., Ltd. The advantage of this approach is a guideline in selecting a suitable thermodynamic model for column design.

Bo et al. [20] studied a new process to separate propylene and propane in ethylene production using the extractive distillation with aqueous acetonitrile (ACN) as the entrainer. A PRO/II software process simulation had been applied with the selection of an appropriate vapor-liquid equilibrium model. A vapor-liquid equilibrium model was confirmed by the experiments and simulation on the existing process, and the novel extractive distillation process was simulated by the PRO/II software. The existing and the new extractive distillation processes were simulated on the basis of the UNIFAC group contribution method. The results of the simulation led to the conclusion that the new process flow scheme was much superior to the existing one with the savings of 13.2% reboiler load, 79.1% condenser load, and the reduction of theoretical trays by 25%. The design of column plates was made according to the simulation results. With the selection of the slant-hole tray according to the design, the radius of plate could be reduced from 5 to 3 m.

The column trays were then designed on the basis of the simulation results for the application in the novel process in practice. The new process, the extractive distillation, required less number of trays, less energy consumption and smaller column diameter. In the design of the distillation column, a new type of multi-overflow compound slant-hole tray was adopted. It had been widely used in the recent years. It is believed that by the new process, the separation of propylene and propane is greatly improved.

Phupaichitkul [5] represented the application of a simulator, PRO/II, to eliminate the limits of capacity expansion or to debottleneck the process. The case study was the topping unit in plant no.2 of the Bangchak Petroleum Public Co., Ltd. The existing unit could handle a slight increase capacity of 45 KBD, but could not handle the higher capacity upto 50 KBD because the expanding capacity overloads the existing equipment design. Thus, the chosen case studies were 50 KBD and 60 KBD. According to the simulation results, bottlenecks occurred in all sections, i.e., separation, heat exchanger network and utility sections of the topping unit.

The separation section, which referred to all distillation columns, required column modifications as follows: internal tray modification to handle slight bottlenecks less than 94% flooding, and random packing replacement that could handle serious bottlenecks. Heat exchanger network (HEN) required the pinch analysis to redesign the new HEN. Adding new units could debottleneck utility sections, which referred to heaters and coolers, usually, in parallel connecting. According to the results of economic evaluation, both capacities of 50 and 60 KBD were economically viable. They yielded high profit rate of about 50% and short payback period for about 2 years. Comparing two alternatives, 50 KBD was more attractive for debottlenecking because of less process bottlenecks involved, which required less modifications.

Chapter 4

Research Methodology

In a chemical process, the transformation of raw materials into desired products usually consists of many unit operations; for example, reaction, separation, mixing, cooling and heating units. These units are combined into a complete process. To model a complete process or a part of it, a simulator is used to generate the model or flowsheet, which is a diagrammatic representation of its unit interconnections, so-called the modeling. The model will predict the products corresponding to the actual operating data for the same feeds and operating conditions, shown in Figure 4.1a. The model or base model represents the actual conditions of the process. It can be used to evaluate process performances [21]. For instance, it predicts how a process would behave if feed flowrate is varied higher than the existing design, shown in Figure 4.1b.

(a) Process modeling
Generate the model or flowsheet which
converts raw materials into desired products.

(b) Process simulation
Simulate the model to predict how a
process would behave if its feeds or
operating conditions were changed.

Figure 4.1 Process modeling and simulation [21]

4.1 Simulation and optimization of the existing debutanizer

With the successful development of a computer model for an existing debutanizer as explained in chapter 3 [19], the operational results of the debutanizer conditions other than the present conditions were simulated and compared so as to improve the debutanizer operation while the basic constraints of the refining operation such as product specifications, etc. were satisfied. So far, a reliable and efficient method to solve the above constraint optimization problems rigorously has not yet been devised. Therefore, in the present work the existing debutanizer will be optimized to a certain degree with the aids of the computer model by relying on a sample trial-and-error scheme.

4.1.1 Choices of operating variables and objectives of optimization

Two major objectives in refinery operation are minimization of energy consumption and maximization of yields of all products, which are reformate and LPG in this work. Therefore, the conditions of operating variables such as feed, fuel gas consumption, reboiler temperature (since the reboiler temperature is not directly available on the simulator, this study will represent the reboiler temperature in terms of reboiler heat duty), condenser duty, reflux ratio, and top column temperature should be investigated. There is no effect due to condenser pressure drop in this case study because no fouling was found during turn around and inspection.

In order to reduce the complexity of the present optimization in operation problem, some of the above variables are fixed, some are resultants, and only the important ones are chosen to be optimized as the operating variables. Accordingly, the optimization of theoretical analogue column in this work assumes that the following variables are fixed:

- Feed properties (41.3 °C, 42 kg/cm^2) and compositions
- Pressure drop across the debutanizer column at 0.177 kg/cm^2
- Top column temperature at 60.57 °C
- Condenser heat duty of 1.1648 Mkcal/h

The resultant variables are:

- Condenser temperature
- Reflux ratio
- Bottom column temperature

And the following operating variables will be investigated:

- Column pressure

- Reboiler heat duty.

Basically, adjustable parameters in controlling the distillation column are pressure and temperature. Thus, the criteria to define column pressure and reboiler heat duty as operating variable is because they are main control variables of the existing debutanizer and are provided by column control facilities on the actual debutanizer. In the case of resultant variables, condenser temperature, reflux ratio and bottom column temperature are the results after the operating parameters were adjusted.

The debutanizer performance will significantly be affected by any change in column pressure and reboiler heat duty. The reformate, LPG, and off gas flowrates are estimated. After a reasonable number of operating conditions have been chosen and the corresponding simulation results are obtained, the economic evaluation is taken to account for the main operating cost in terms of the fuel cost of the fired-heater type reboiler, as well as the product values of reformate, LPG and off gas.

4.1.2 Product specifications

Any change in the operating variables (column pressure and reboiler heat duty) will naturally affect product quality to some extent. The operating conditions that yield product in specifications will be evaluated economically. The product specifications used to determine the suitability or acceptability of the operating conditions are shown in Table 4.1.

It should be noted from the product specifications that not only the hard specification must be considered but other properties, for example, C_2 in LPG, etc. should also be monitored. However, end point and octane number of the reformate are not of interest in this work. Since the end point of the reformate and octane number are negligibly affected by adjustable operating variables. The main significant properties considered as hard specification is Reid vapor pressure of the reformate. In case of LPG, since the production of LPG from the debutanizer is only a small portion of the refinery LPG pool, therefore, LPG specification will not be considered as the hard specification and can be ignored in this work. There is no specification of off gas because it will be used as the refinery fuel.

Table 4.1 Product specifications of the existing debutanizer

Product	Specification	
1. Reformate	Reid vapor pressure ASTM D 5191	3.92 – 5.22 psi (27 – 36 kPa)
	Octane number ASTM D 2699	99 - 102
	End point ASTM D86	205 °C
2. LPG	C_5^+ ASTM D 2163	2.0 vol % max.

In any refinery plant, the specification of off gas has no importance.

4.2 Simulation procedures

In this work, the existing debutanizer is firstly modeled as the base case model. This base case model, subsequently, is used for the optimization of a higher economic benefit. The simulation and optimization procedures consist of three steps as follows:

- Setting the simulation model of the existing debutanizer
- Find a representative simulation model or a base case of the debutanizer
- Optimization and economic evaluation

4.2.1 Setting the simulation model of the existing debutanizer

The process flow diagram of the debutanizer including the streams of feed and products as shown in Figure 1.1 was defined. The components and physical properties of each stream and the process conditions such as operating conditions, tray efficiency, temperature profiles, etc. were listed. The proper thermodynamic method, which is the critically important step to find the simulation solution, was selected.

The important potential consideration to choose the proper physical property models of the debutanizer is using an appropriate vapor-liquid equilibrium. For reformate and LPG separation, which is a relative easy hydrocarbon separation, the relative volatility can be expressed by the following equation [22],

$$\alpha_{ij} = \frac{K_{LT}Key}{K_{HY}Key} \tag{4.1}$$

Where α_{ij} is the relative volatility of light to heavy key components. K_{LT} *Key* is the equilibrium constant of the light key component and K_{HY} *Key* is the equilibrium constant of the heavy key component. If the relative volatility is about 2, a cubic equation of state such as the Soave Redlich Kwong (SRK) or Peng-Robinson (PR) is recommended for modeling of stage [18]. A check of the experimental data indicated that both the SRK and PR models gave similar results at any α_{ij} [19]. However, the cubic equation SRK model is applied in this work because it gives higher accuracy simulation results than the PR model. The number of theoretical trays is also an important consideration in simulation. The number of theoretical trays has to be determined from the number of actual trays. A good rough estimation is expressed by the Fenske's equation [22].

$$N_{m+1} = \log\left[\left(\frac{LTKey}{HYKey}\right)_D \times \left(\frac{HYKey}{LTKey}\right)_W\right] / \log\alpha_{ij} \tag{4.2}$$

where:

N_{m+1} = Minimum number of theoretical trays

LT Key = Fraction of the selected light key

HY Key = Fraction of the selected heavy key

D = Fraction of selected key in the distillate product

W = Fraction of selected key in the bottom product

The estimated tray efficiency of the debutanizer is referred to the typical overall tray efficiency [17]. The tray efficiency is used to convert the number of actual trays to theoretical stages. The tray efficiency is assumed uniform, unless there is good reason to assume different efficiencies of the top and bottom sections, i.e., tray flooding and tray damage.

The above-described items have to be well defined before the simulation starts [23]. The flowrate, temperature and pressure of every stream of the column were measured. The temperature and pressure or heat duty of the reboiler and condenser were obtained from the actual conditions. The devices to measure such parameters had to be calibrated. The debutanizer simulation model was then run. The results are given in Chapter 5.

4.2.2 Find a representative simulation model or a base case of the debutanizer

The simulator was used to find a base case from the simulation models of the debutanizer based on the actual data by verifying a base case from actual operating data; the actual operating data must be tested for its validity. Some parameters must be adjusted to correspond the predicted data of the base case with the actual data. These parameters include flowrate of products, reflux ratio, temperature profiles and product specifications with their compositions. After a base case matches the predicted data with the actual data, it can be used for the optimization.

The debutanizer simulation model was run and the base case model, which represents the actual conditions of the debutanizer, was established. The mentioned logic is valid only if the simulation reflects the actual performance, i.e., plant data. The test runs and model tuning were done under the normal operating conditions to confirm the simulation accuracy, reliability and consistency by checking the calculation of material and component balances, i.e., the feed flowrate, the product flowrates and the compositions [11]. The simulated reflux ratio, reboiler heat duty, column temperature and composition profiles will be compared with the measured data [18]. In a good simulation, the overall tower performance is determined from field measurements by adjusting the number of stages in the simulation until the simulation matches the measured compositions, temperature profiles and flow. If the simulated reflux ratio and reboiler heat duty exceed the measured values, the actual column efficiency is higher than the estimated one and the number of simulation stages must be increased. Likewise, if those simulated values are less than the measured reflux ratio and reboiler heat duty, the efficiency and theoretical number of stages must be lowered. When the simulated reflux rate and reboiler heat duty match the measured values, the simulation model is accepted as the representative model, and the composition profiles are determined.

4.2.3 Optimization and economic evaluation

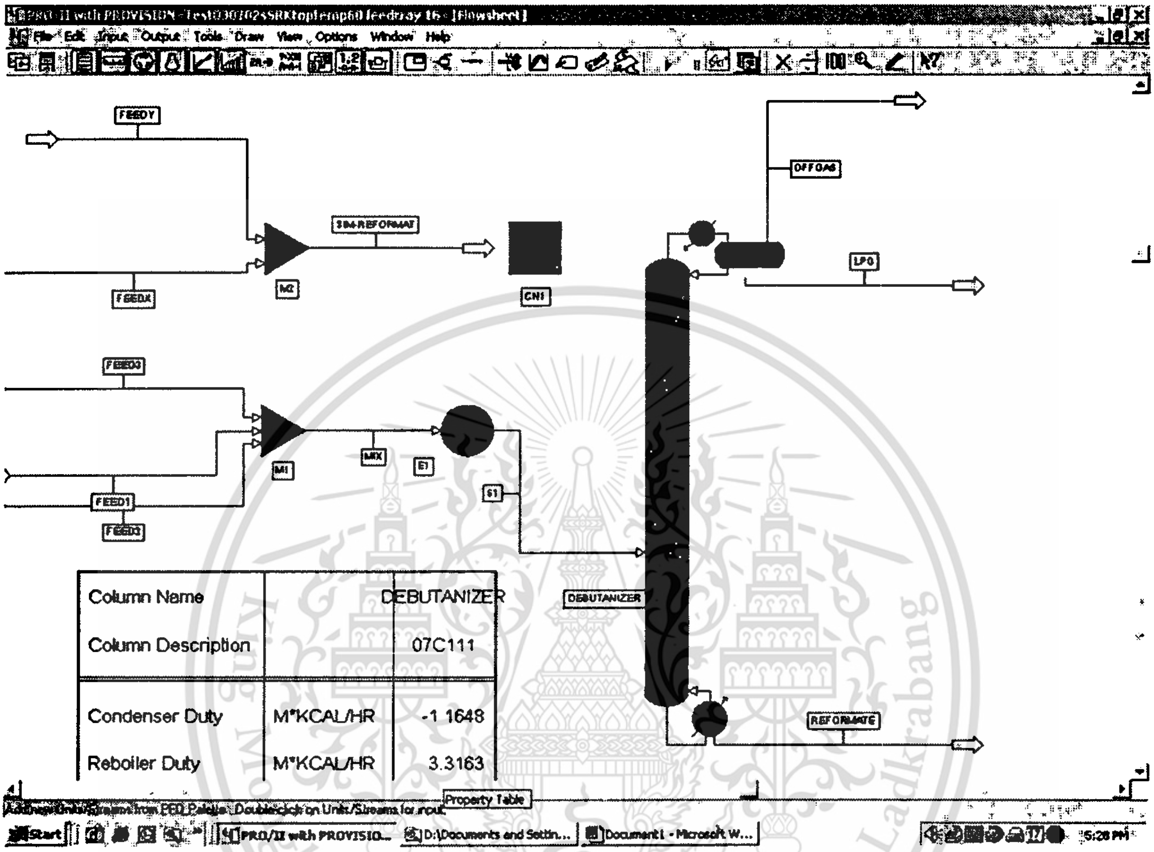
The model is used to observe the response of the existing debutanizer after applying the operating conditions, i.e., column pressure and reboiler heat duty. All analysis methods mentioned above can be used to identify the parameters of the debutanizer to achieve economic benefits. As mentioned earlier, the objectives of the optimization consists of two major items. The first is to decrease the operating costs associated with fuel cost compared with the existing operating condition. The second is the change in the product values of reformate, LPG, and off gas to suit the current market demand. The simulation in this work is limited to maximize the reformate and LPG due to their attractive prices. The cost of energy consumption of each simulated case was varied. Other operating costs, for example, energy consumption of pumps and fin-fan condensers were fixed. The economic benefit is calculated as follows (more details are shown in Appendix A),

Economic benefit = Benefit (any case) – Benefit (a base case),

Objective function (Benefit) = Total product values – Energy consumption cost (fuel gas)

In addition, the amount of the C_5^+ in LPG was also studied by changing 8th-tray's temperature.

Figure 4.2 shows the simulation flowsheet of the existing debutanizer that was simulated as a base case used in this work.



Column Name		DEBUTANIZER
Column Description		07C111
Condenser Duty	M*KCAL/HR	-1 1648
Reboiler Duty	M*KCAL/HR	3.3163

Figure 4.2 PRO/II simulation flowsheet of the existing debutanizer

Chapter 5

Results and Discussion

The results are divided into 2 parts. First, the simulation results of PRO/II are discussed and compared with the actual data from the existing debutanizer. Second, the results of the optimization are suggested. The effects of the operating conditions, i.e., column pressure and reboiler heat duty on products and product quality are discussed.

5.1 Simulation results

To check and tune the simulation model for the debutanizer, the simulation results of a base case are compared with the actual data and shown in Table 5.1.

Table 5.1 Comparison of the simulation results of the base case with the actual data

Item	Simulated data	Actual data*	% Deviation
1. Compositions (mole fraction)			
1.1 Off gas			
Hydrogen	0.3275	0.3188	2.64
Methane	0.0426	0.0406	4.67
Ethane	0.1871	0.1866	0.27
Propane	0.2957	0.2843	3.82
n-Butane	0.0530	0.0578	8.23
iso-Butane	0.0921	0.1008	8.55
1.2 LPG			
Propane	0.3475	0.3506	0.89
n-Butane	0.2298	0.2132	7.21
iso-Butane	0.3027	0.3010	0.54

Table 5.1 Comparison of the simulation results of the base case with the actual data (cont.)

Item	Simulated data	Actual data*	% Deviation
1. Compositions (mole fraction)			
1.3 Reformate			
Reid vapor pressure (RVP), psi	4.21	4.22	0.24
2. Flowrate (kg/h)			
Feed	73,282.17	73,851.91	0.77
Reformate	67,138.10	67,204.29	0.09
LPG	3,414.39	3,441.48	0.78
Off gas	2,729.68	2,636.10	3.43
3. Temperature profiles (°C)			
Overhead	32.00	31.80	0.62
Top tray	60.57	60.49	0.13
8th-tray	94.96	94.85	0.12
22nd-tray	173.58	173.81	0.13
Bottoms	218.60	219.00	0.18
4. Miscellaneous			
Reflux ratio	3.60	3.50	2.77
Reboiler heat duty (10^6 kcal/h)	3.32	3.63	9.47
Column pressure (kg/cm^2, absolute)	13.5	13.5	0

* At steady-state condition

Table 5.1 compares percent deviations obtained between PRO/II simulation and the actual data. The compositions, flowrates of each stream and temperature profiles results from PRO/II simulation agree with those from the actual data. The deviation between the simulation results and the actual data are not more than 10%, which are in a reasonable and acceptable range. As a result, it can be assumed that the base case from the simulation models can represent the actual performance of the existing debutanizer of this refinery plant. The simulation is a reliable basis for optimization and troubleshooting.

This base case is use to simulate different conditions in order to find the optimum operating conditions. The simulation results of different operating conditions are shown in Tables 5.2 –5.6. Column pressure affects boiling points or separation of key components. Tables 5.2 and 5.3 summarize all operating conditions investigated when column pressure is changed at constant reformate RVP of 4.21 psi and constant reboiler heat duty of 3.3163 x10^6 kcal/h. As the matter of fact, the column pressure affects condensation, vaporization, temperature profiles, compositions and volatilities of components. LPG flowrate increases when column pressure increases because usually the column pressure control is integrated with the condensation system. Light components will be induced to reformate when pressure increases so as the reformate flowrate increases.

From Tables 5.4 –5.6, the effect of reboiler heat duty is discussed. A change in the reformate. For instance, a decrease in reboiler heat duty leads to a rise in concentration of light key components in reformate, reformate RVP and flowrate while overhead products decreases.

Table 5.2 The simulation results at constant reformate RVP of 4.21 psi

Column pressure (kg/cm^2, absolute) 1. Compositions (mole fraction)	11.5	12.5	13.5	14.5	15.5
1.1 Off gas					
Hydrogen	0.3059	0.3160	0.3275	0.3406	0.3532
Methane	0.0402	0.0413	0.0426	0.0440	0.0453
Ethane	0.1825	0.1846	0.1871	0.1897	0.1919
Propane	0.2983	0.2971	0.2957	0.2941	0.2939
n-Butane	0.0555	0.0542	0.0530	0.0512	0.4942
iso-Butane	0.0939	0.0929	0.0921	0.0918	0.0912
1.2 LPG					
Propane	0.3324	0.3399	0.3475	0.3550	0.3618
n-Butane	0.2266	0.2276	0.2298	0.2304	0.2312
iso-Butane	0.2922	0.2976	0.3027	0.3083	0.3135
1.3 Reformate					
2. Flowrate (kg/h)					
Reformate	67,081.36	67,102.01	67,138.10	67,165.56	67,202.45
LPG	3,189.40	3,304.36	3,414.39	3,531.39	3,643.39
Off gas	3,011.41	2,875.80	2,729.68	2,585.22	2,436.33
3. Temperature profiles (°C)					
Overhead	30.89	31.53	32.00	32.16	32.33
Top tray	60.57	60.57	60.57	60.57	60.57
8th-tray	103.06	98.96	94.96	90.11	86.62
22nd-tray	168.33	171.08	173.58	176.84	179.67
Bottoms	211.48	215.22	218.60	223.58	227.78
4. Miscellaneous					
Reflux ratio	3.48	3.51	3.60	3.74	3.87
Reboiler heat duty (10^6 kcal/h)	2.89	3.16	3.32	3.50	3.79

Table 5.3 The simulation results at constant reboiler heat duty of 3.3163 x10^6 kcal/h (the relaxed reformate RVP case)

Column pressure (kg/cm^2, absolute) / 1. Compositions (mole fraction)	11.5	12.5	13.5	14.5	15.5
1.1 Off gas					
Hydrogen	0.2918	0.3084	0.3275	0.3485	0.3729
Methane	0.0381	0.0403	0.0426	0.0449	0.0477
Ethane	0.1735	0.1802	0.1871	0.1940	0.2010
Propane	0.2892	0.2929	0.2957	0.2909	0.2828
n-Butane	0.0619	0.0575	0.0530	0.0477	0.0427
iso-Butane	0.1029	0.0982	0.0921	0.0844	0.0760
1.2 LPG					
Propane	0.3099	0.3290	0.3475	0.3635	0.3764
n-Butane	0.2477	0.2385	0.2298	0.2203	0.2109
iso-Butane	0.3084	0.3075	0.3027	0.2959	0.2857
1.3 Reformate					
Reid vapor pressure (RVP), psi	2.87	3.52	4.21	4.97	5.75
2. Flowrate (kg/h)					
Reformate	66,021.64	66,596.73	67,138.10	67,640.10	68,111.56
LPG	2,984.14	3,209.37	3,414.39	3,617.39	3,927.60
Off gas	4,277.20	3,476.88	2,729.68	2,024.68	1,243.82
3. Temperature profiles (°C)					
Overhead	33.01	32.67	32.00	31.39	30.97
Top tray	60.57	60.57	60.57	60.57	60.57
8th-tray	97.56	95.91	94.96	93.90	94.41
22nd-tray	175.47	174.08	173.58	172.57	170.64
Bottoms	215.68	217.20	218.60	219.99	221.18
4. Miscellaneous					
Reflux ratio	3.93	3.77	3.60	3.40	3.17

Table 5.4 The simulation results at column pressure of 12.5 kg/cm^2 with different reboiler heat duties

Reboiler heat duty (10^6 kcal/h) / 1. Compositions (mole fraction)	2.72	2.82	2.92	3.02	3.12	3.22	3.32	3.42	3.52
1.1 Off gas									
Hydrogen	0.3882	0.3711	0.3559	0.3421	0.3297	0.3184	0.3084	0.2993	0.2911
Methane	0.0506	0.0485	0.0466	0.0448	0.0433	0.0419	0.0403	0.0391	0.0390
Ethane	0.2118	0.2057	0.1999	0.1945	0.1894	0.1845	0.1802	0.1761	0.1724
Propane	0.2894	0.2940	0.2965	0.2971	0.2965	0.2950	0.2929	0.2904	0.2878
n-Butane	0.0386	0.0413	0.0442	0.0473	0.0505	0.0539	0.0575	0.0609	0.0644
iso-Butane	0.0683	0.0730	0.0780	0.0833	0.0886	0.0936	0.0982	0.1021	0.1055
1.2 LPG									
Propane	0.3771	0.3712	0.3636	0.3552	0.3464	0.3376	0.3290	0.3209	0.3134
n-Butane	0.2032	0.2033	0.2088	0.2151	0.2222	0.2299	0.2385	0.2477	0.2570
iso-Butane	0.2619	0.2686	0.2763	0.2846	0.2929	0.3006	0.3075	0.3132	0.3176
1.3 Reformate									
Reid vapor pressure (RVP), psi	5.34	5.04	4.69	4.37	4.07	3.79	3.52	3.27	3.04
2. Flowrate (kg/h)									
Reformate	67,534.27	67,370.28	67,210.68	67,054.27	66,895.98	66,746.59	66,596.73	66,452.87	66,322.88
LPG	2,825.29	2,887.91	2,960.07	3,024.00	3,077.81	3,134.75	3,209.37	3,208.50	3,225.19
Off gas	2,922.61	3,023.98	3,111.42	3,203.89	3,308.37	3,400.82	3,476.88	3,620.80	3,734.09
3. Temperature profiles (°C)									
Overhead	29.91	30.18	30.35	31.10	31.53	32.03	32.67	33.06	33.45
Top tray	60.57	60.57	60.57	60.57	60.57	60.57	60.57	60.57	60.57
8th-tray	102.86	101.84	100.53	99.20	98.00	96.89	95.91	94.86	93.77
22nd-tray	165.05	166.45	167.86	169.37	170.87	172.37	174.08	175.96	176.94
Bottoms	207.99	209.80	210.79	212.49	214.10	215.70	217.20	218.59	219.99
4. Miscellaneous									
Reflux ratio	3.17	3.25	3.37	3.47	3.57	3.67	3.77	3.87	3.97

Table 5.5 The simulation results at column pressure of 13.5 kg/cm^2 with different reboiler heat duties

Reboiler heat duty (10^6 kcal/h) 1. Compositions (mole fraction)	2.91	3.01	3.11	3.22	3.32	3.42	3.52
1.1 Off gas							
Hydrogen	0.3858	0.3688	0.3533	0.3398	0.3275	0.3164	0.3065
Methane	0.0498	0.0477	0.0458	0.0441	0.0426	0.0412	0.0400
Ethane	0.2082	0.2024	0.1970	0.1919	0.1871	0.1828	0.1788
Propane	0.2854	0.2907	0.2940	0.2954	0.2957	0.2965	0.2980
n-Butane	0.0399	0.0429	0.0460	0.0494	0.0530	0.0565	0.0600
iso-Butane	0.0698	0.0749	0.0806	0.0864	0.0921	0.0973	0.1020
1.2 LPG							
Propane	0.3750	0.3697	0.3631	0.3555	0.3475	0.3396	0.3319
n-Butane	0.2024	0.2080	0.2145	0.2217	0.2298	0.2382	0.2470
iso-Butane	0.2660	0.2742	0.2834	0.2932	0.3027	0.3115	0.3193
1.3 Reformate							
Reid vapor pressure (RVP), psi	5.52	5.17	4.83	4.51	4.21	3.95	3.69
2. Flowrate (kg/h)							
Reformate	67,750.68	67,594.27	67,438.98	67,286.59	67,138.10	66,995.87	66861.88
LPG	3,198.07	3,263.00	3,322.81	3,373.76	3,414.39	3,447.50	3468.19
Off gas	2,333.42	2,424.90	2,520.37	2,621.82	2,729.68	2,838.80	2952.05
3. Temperature profiles (°C)							
Overhead	29.75	30.35	30.89	31.49	32.00	32.54	32.96
Top tray	60.57	60.57	60.57	60.57	60.57	60.57	60.57
8th-tray	99.61	98.38	97.22	96.05	94.96	92.11	89.63
22nd-tray	167.83	169.24	170.66	172.17	173.58	175.07	176.66
Bottoms	212.15	213.84	215.50	217.11	218.6	220.08	221.47
4. Miscellaneous.							
Reflux ratio	3.22	3.31	3.40	3.49	3.60	3.69	3.80

Table 5.6 The simulation results at column pressure of 14.5 kg/cm^2 with different reboiler heat duties

Reboiler heat duty (10^6 kcal/h) 1. Compositions (mole fraction)	3.22	3.32	3.42	3.52	3.62	3.72
1.1 Off gas						
Hydrogen	0.3643	0.3485	0.3347	0.3236	0.3164	0.3158
Methane	0.0467	0.0449	0.0421	0.0407	0.0398	0.0397
Ethane	0.1989	0.1940	0.1939	0.1896	0.1867	0.1866
Propane	0.2869	0.2909	0.2931	0.2939	0.2941	0.2944
n-Butane	0.0442	0.0477	0.0511	0.0544	0.0564	0.0574
iso-Butane	0.0843	0.0844	0.0903	0.0959	0.1003	0.1024
1.2 LPG						
Propane	0.3754	0.3635	0.3567	0.3503	0.3462	0.3438
n-Butane	0.2130	0.2203	0.2279	0.2356	0.2400	0.2403
iso-Butane	0.2852	0.2959	0.3066	0.3171	0.3265	0.3341
1.3 Reformate						
Reid vapor pressure (RVP), psi	5.29	4.97	4.65	4.38	4.18	3.91
2. Flowrate (kg/h)						
Reformate	67,788.59	67,640.1	67,496.87	67,367.88	67,220.26	67,073.31
LPG	3,576.76	3,617.39	3,648.50	3,675.20	3,748.70	3,827.42
Off gas	1,916.82	2,024.68	2,136.80	2,239.10	2,313.21	2,381.44
3. Temperature profiles (°C)						
Overhead	30.95	31.39	31.68	32.15	32.69	33.23
Top tray	60.57	60.57	60.57	60.57	60.57	60.57
8th-tray	95.27	93.90	91.98	89.34	88.26	87.25
22nd-tray	171.17	172.57	173.95	174.00	174.78	175.33
Bottoms	217.71	219.99	221.37	222.76	223.65	224.66
4. Miscellaneous						
Reflux ratio	3.29	3.40	3.51	3.63	3.77	3.94

5.2 Optimization results

5.2.1 Effect of debutanizer column pressure

The simulation started from the data of base case. The maximum column pressure in this study is 15.5 kg/cm^2 (absolute) regarding to the design. The effect of column pressure on the reformate flowrate and fuel gas consumption at constant reformate RVP (Reid vapor pressure) of 4.21 psi (a base case), shown in Figure 5.1. The reformate flowrate slightly increases as the column pressure increases. This result indicates that when the column pressure increases, more reboiler heat duty or fuel gas consumption is needed to keep the reformate RVP constant. This figure shows a slight effect of column pressure on the reformate flowrate at constant reformate RVP. Figure 5.2 illustrates that the LPG flowrate increases with an increase in column pressure. It can be explained that when the column pressure is raised, the condensation of LPG from the overhead vapors increases, on the other hand off gas decreases.

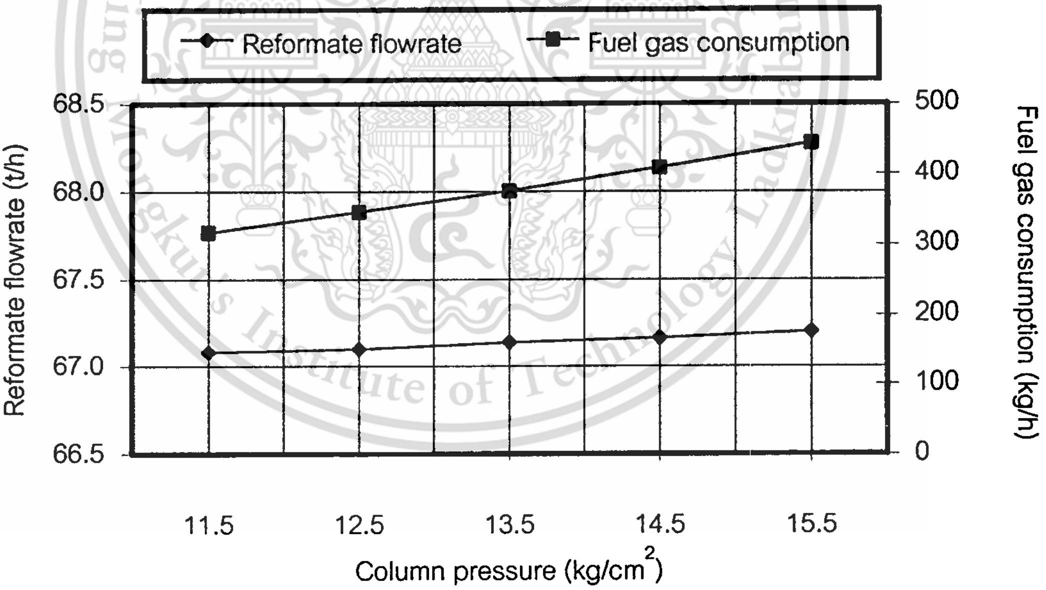


Figure 5.1 Effect of column pressure on reformate flowrate and fuel gas consumption at constant reformate RVP of 4.21 psi

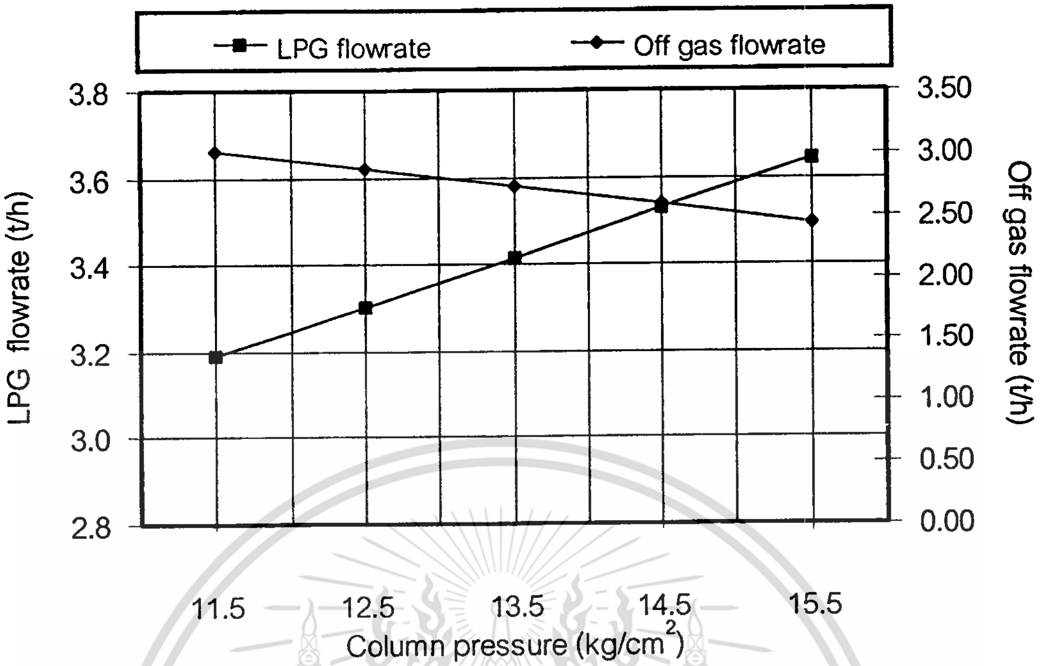


Figure 5.2 Effect of column pressure on LPG and off gas flowrates at constant reformate RVP of 4.21 psi

Figure 5.3 shows fuel gas consumption and economic benefit as a function of column pressure. From Figure 5.3, an increase in column pressure leads to a slight increase in economic benefit since in this case the economic benefit is mostly obtained from LPG production. When the column pressure is higher than 13.5 psi, the positive benefit is achieved. Because the economic benefit is low, and the separations of reformate and LPG at higher column pressure is more difficult than at a lower column pressure so this simulation method is not of economic interest.

Figure 5.4 shows the increases in reformate flowrate and refomate RVP when column pressure increases at reboiler heat duty of 3.3163x10^6 kcal/h (a base case). This case or in other words "the relaxed reformate RVP case", the reformate RVP must be monitored within specification of 3.92-5.22 psi. The reformate RVP of more than 5.22 psi will cause vaporization during use to gasoline due to its high gas or light-end content.

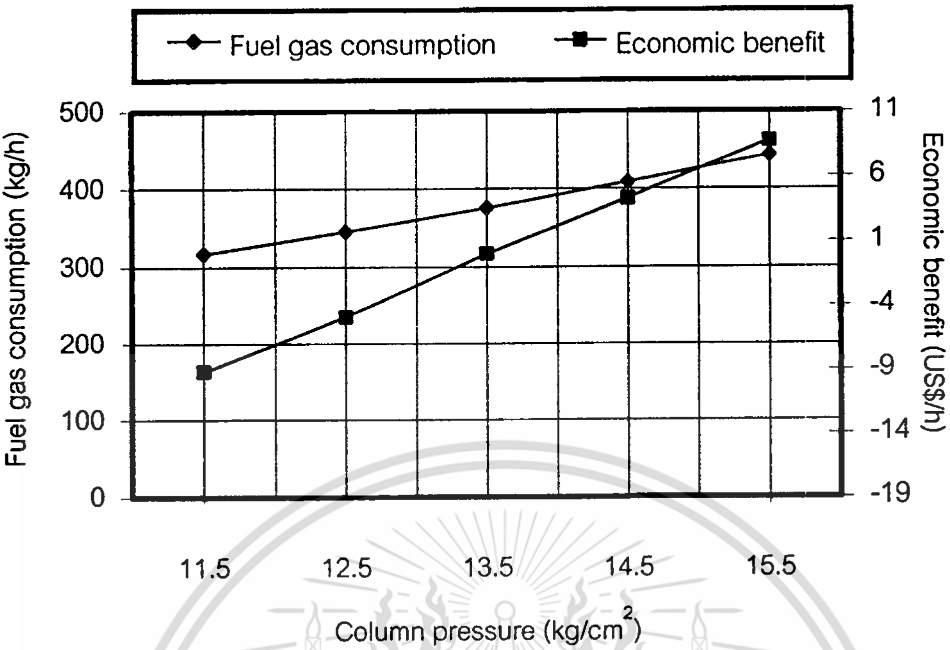


Figure 5.3 Effect of column pressure on fuel gas consumption and economic benefit at constant reformate RVP of 4.21 psi

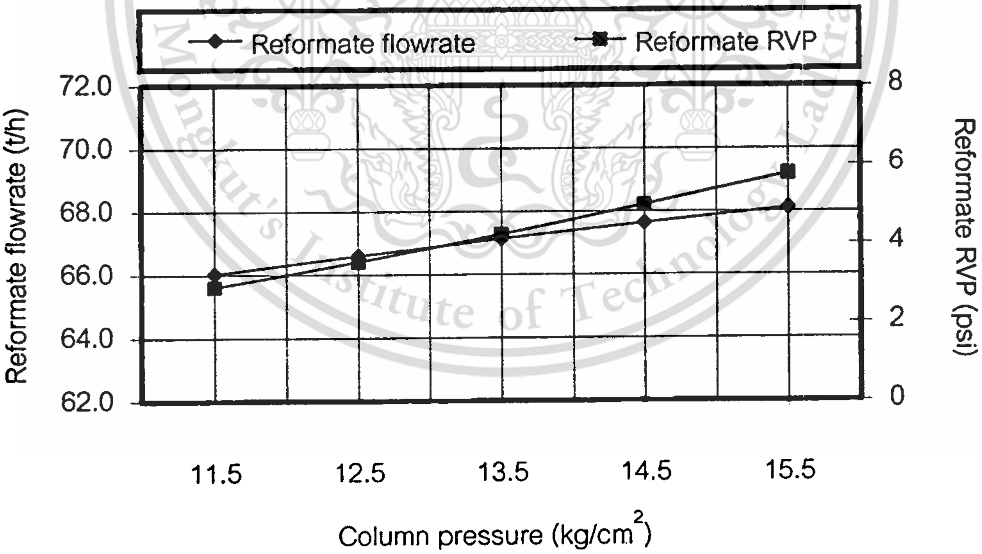


Figure 5.4 Effect of column pressure on reformate flowrate and reformate RVP at constant reboiler heat duty of 3.3163 x 10^6 kcal/h

Figure 5.5 indicates that the LPG flowrate increases as an increase in column pressure while off gas significantly decreases due to the decrease in overhead vapors and more condensation of LPG fraction when column pressure increases at constant reboiler heat duty.

The economic benefit result and the reformate RVP is shown in Figure 5.6. The economic benefit increases sharply if higher reformate flowrate is achieved by increasing the column pressure with constant reboiler heat duty and leaving the reformate RVP high. Due to the constraint in the reformate RVP value, therefore, it should not more than 5.22 psi, at which the column pressure is about 15 kg/cm^2. The maximum column pressure is designed at 15.5 kg/cm^2 as mentioned earlier in section 5.2.1. Therefore, for a safe operation the recommended column pressure should be 14.5 kg/cm^2.

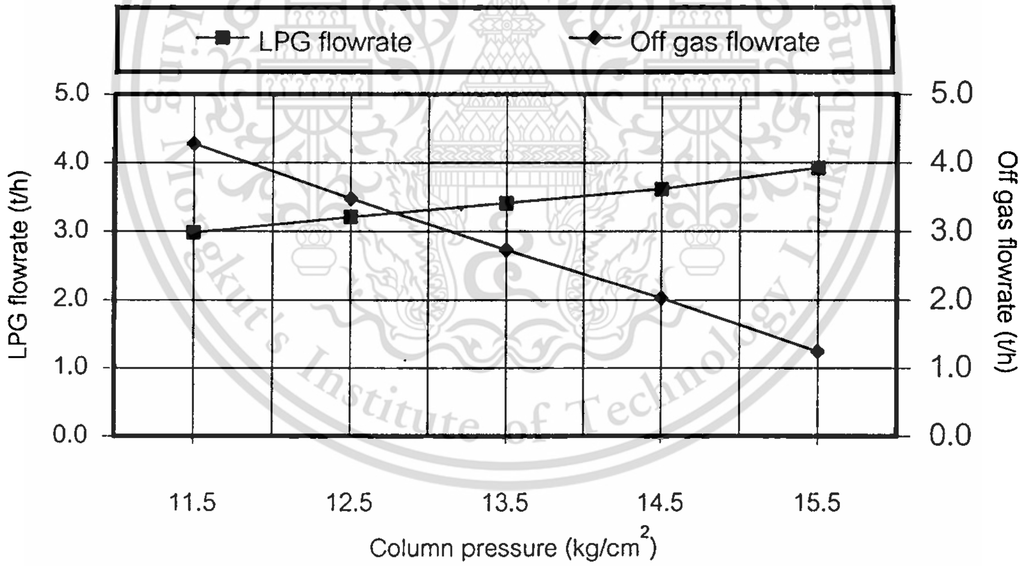


Figure 5.5 Effect of column pressure on LPG flowrate and off gas flowrate at constant reboiler heat duty of 3.3163 x 10^6 kcal/h

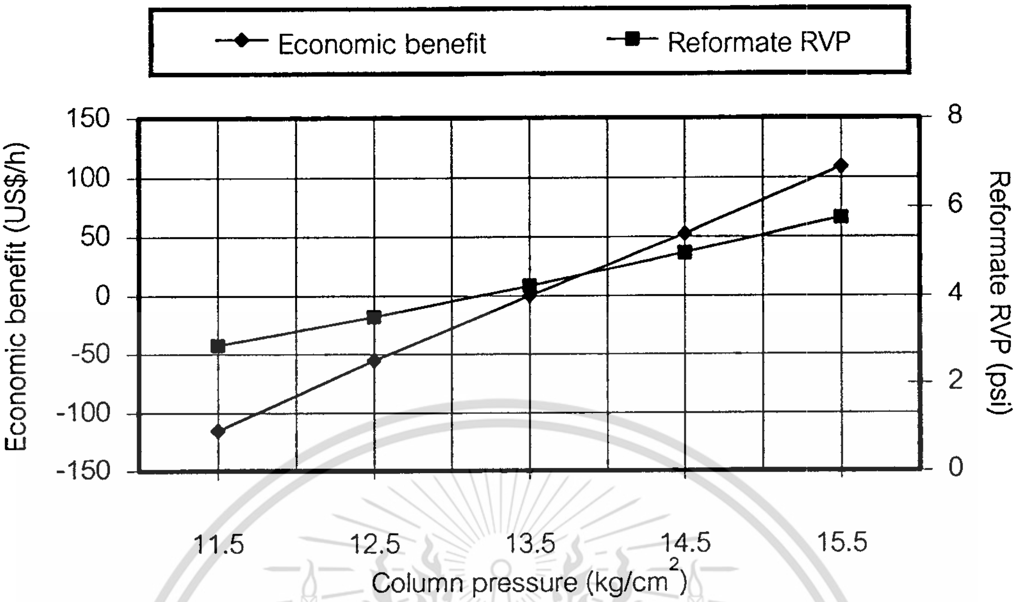


Figure 5.6 Effect of column pressure on economic benefit and reformate RVP at constant reboiler heat duty of 3.3163×10^6 kcal/h

Figure 5.7 is used to compare the economic benefit of two cases: 1) constant the reformate RVP of 4.21 psi by increasing reboiler heat duty, and 2) increasing reformate RVP or relaxed reformate RVP at constant reboiler heat duty of 3.3163×10^6 kcal/h. It shows that the relaxed reformate RVP case has higher economic benefit, although the positive economic benefit starts at the column pressure greater than 13.5 kg/cm^2. The case of relaxed reformate RVP is more interesting than the case of constant reformate RVP of 4.21 psi, but the reformate RVP has to be monitored within specification (not grater than 5.22 psi).

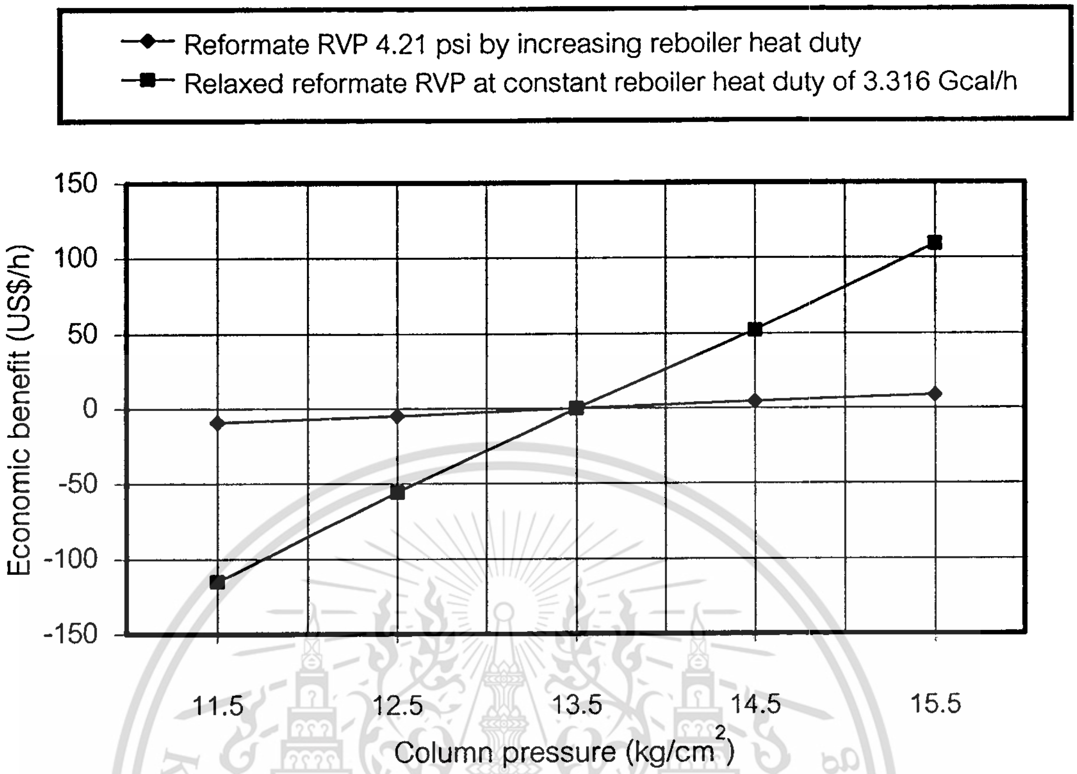


Figure 5.7 Effect of column pressure on economic benefit at constant reformate RVP of 4.21 psi and relaxed reformate RVP

5.2.2 Effect of reboiler heat duty at constant column pressure

The effect of reboiler heat duty at column pressure of 13.5 kg/cm^2 on the reformate flowrate and the reformate RVP is shown in Figure 5.8. In this case, lower reformate flowrate as well as reformate RVP are obtained at the higher reboiler heat duty. The reformate RVP is high at a higher fraction of the light-end products. The reformate RVP must be monitored and controlled not more than 5.22 psi. The flowrates of LPG and off gas are slightly enhanced by increasing reboiler heat duty as shown in Figure 5.9. This is because there are more overhead vapors at a higher reboiler heat duty. The net economic benefit decreases when reboiler heat duty increases as shown in Figure 5.10 since the decrease in reformate significantly affects the economic benefit. The positive economic benefit is obtained when the reboiler heat duty is less than 3.3163 x 10^6 kcal/h.

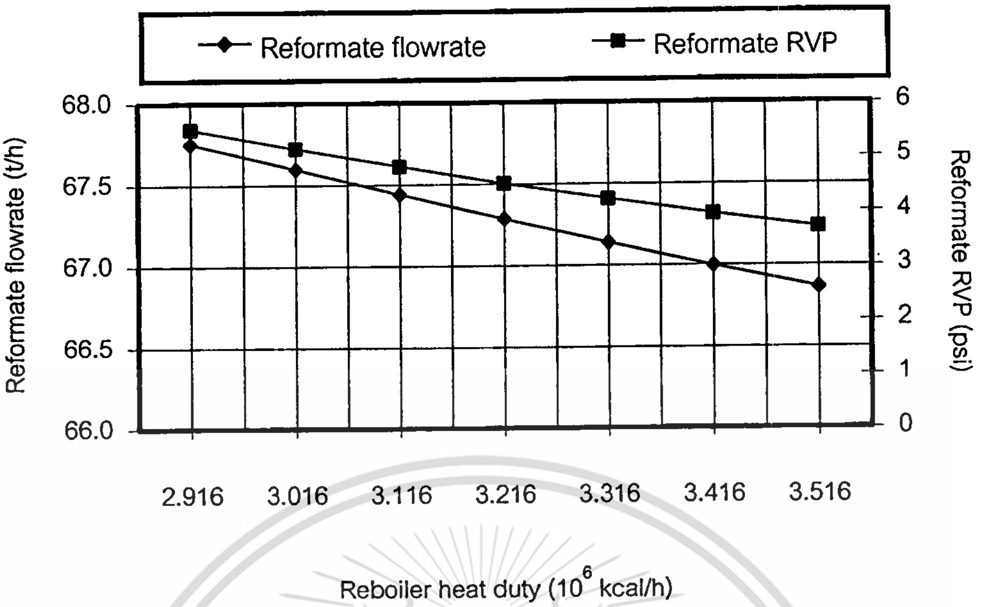


Figure 5.8 Effect of reboiler heat duty on reformate flowrate and reformate RVP at column pressure of 13.5 kg/cm^2

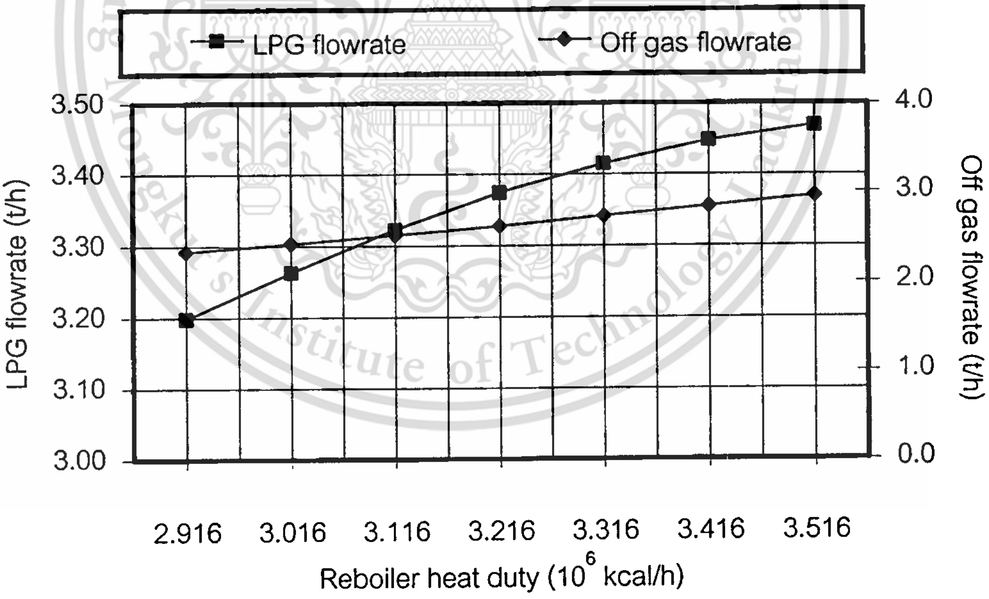


Figure 5.9 Effect of reboiler heat duty on LPG and off gas flowrates at column pressure of 13.5 kg/cm^2

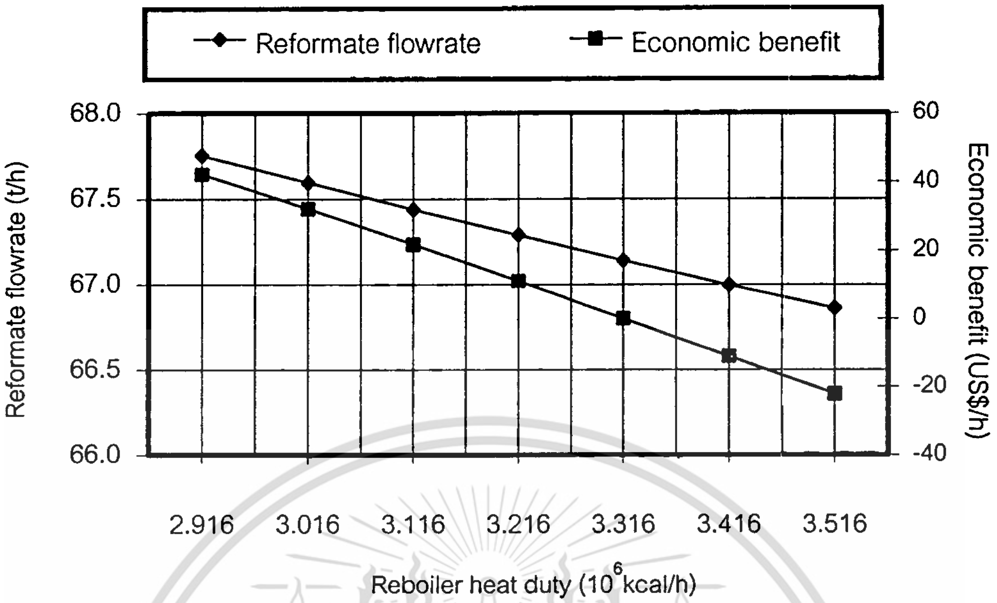


Figure 5.10 Effect of reboiler heat duty on reformate flowrate and economic benefit at column pressure of 13.5 kg/cm^2

Studying the effect of reboiler heat duty at different column pressures is also worth investigated. Figures 5.11, 5.12 and 5.13 show the results of the column pressures of 12.5, 13.5 and 14.5 kg/cm^2. The maximum studied column pressure is 14.5 kg/cm^2 due to safty operation. Figures 5.11 and 5.13 show the same results as in Figures 5.8 and 5.10. At any particular reboiler heat duty, the reformate flowrate increases when column pressure increases. Operating at the higher column pressure results in higher economic benefit. A column pressure of 14.5 kg/cm^2 will achieve a greater economic benefit than column pressures of 13.5 and 12.5 kg/cm^2. According to the reformate RVP specification, the results in Figures 5.11 and 5.13 show that the accepted reboiler heat duties at column pressure of 14.5 kg/cm^2 are 3.2364 – 3.7163 x 10^6 kcal/h. The greatest economic benefit is achieved at column pressure of 14.50 kg/cm^2 and reboiler heat duty of 3.2364 x 10^6 kcal/h, which confirmed the results of previous section.

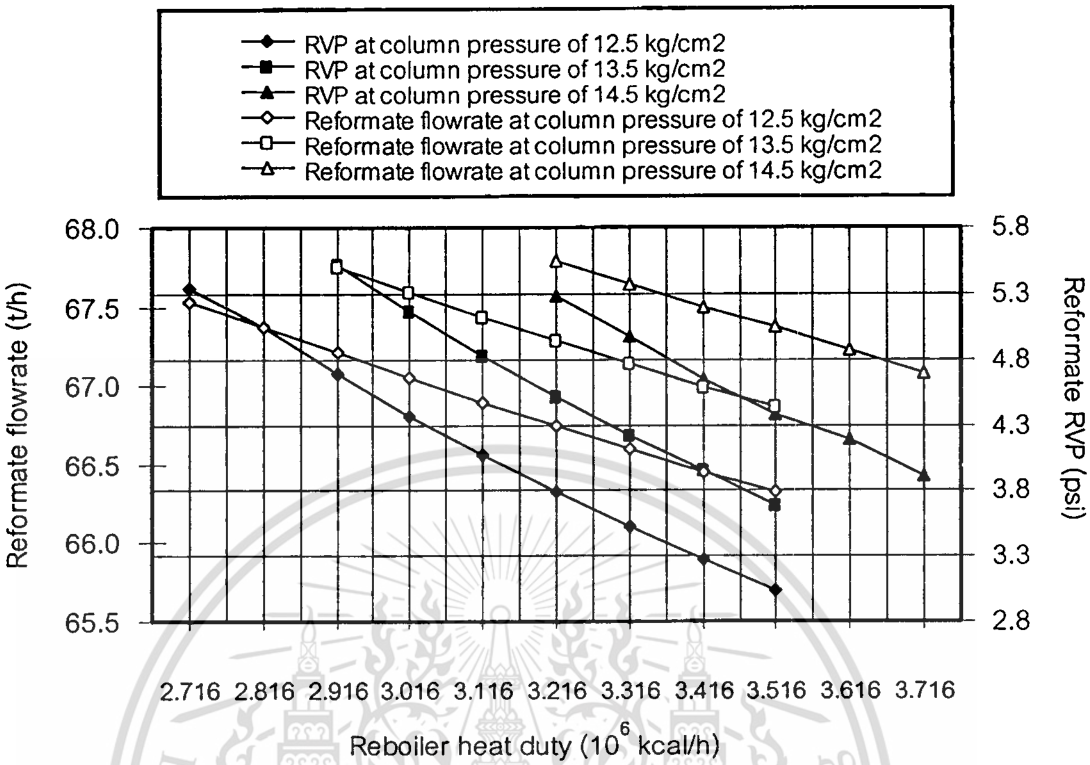


Figure 5.11 Effect of reboiler heat duty on reformate flowrate and reformate RVP at different column pressures

At every column pressure, an increase in reboiler heat duty results in an increase in LPG flowrate as well as off gas flowrate. At the same reboiler heat duty, a higher column pressure results in a higher flowrate of LPG but lower flowrate of off gas.

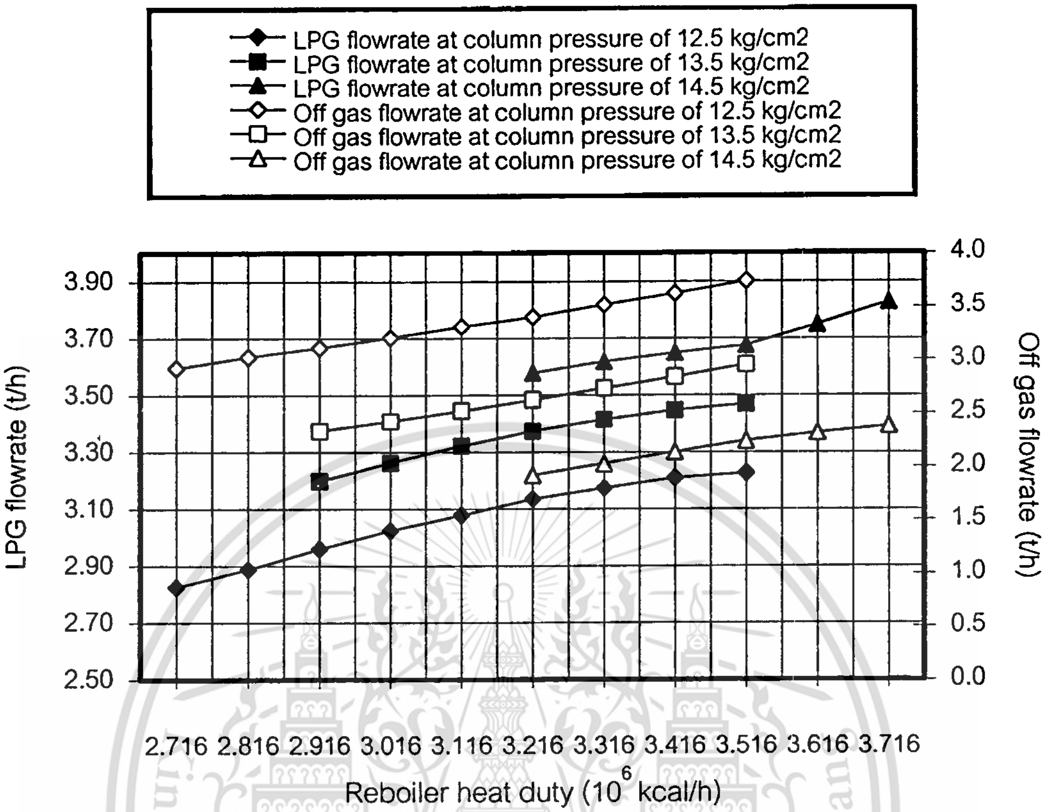


Figure 5.12 Effect of reboiler heat duty on LPG and off gas flowrats at different column pressures

5.2.3 Effect of the 8th-tray's temperature on C_5^+ content in LPG

Figure 14 illustrates the C_5^+ content in LPG and reformate RVP for various temperatures in 8th tray. The C_5^+ content increases significantly when 8th-tray temperature increased. It can be concluded that when temperature increases higher heavy fraction (heavy key component: C_5^+) will be vaporized into overhead product resulting in more amount of C_5^+ in LPG. The change of C_5^+ in column appears to be a very small effect to reformate RVP. More C_5^+ in LPG impacts LPG specification as the C_5^+ in LPG must lower than 2.0 vol%.

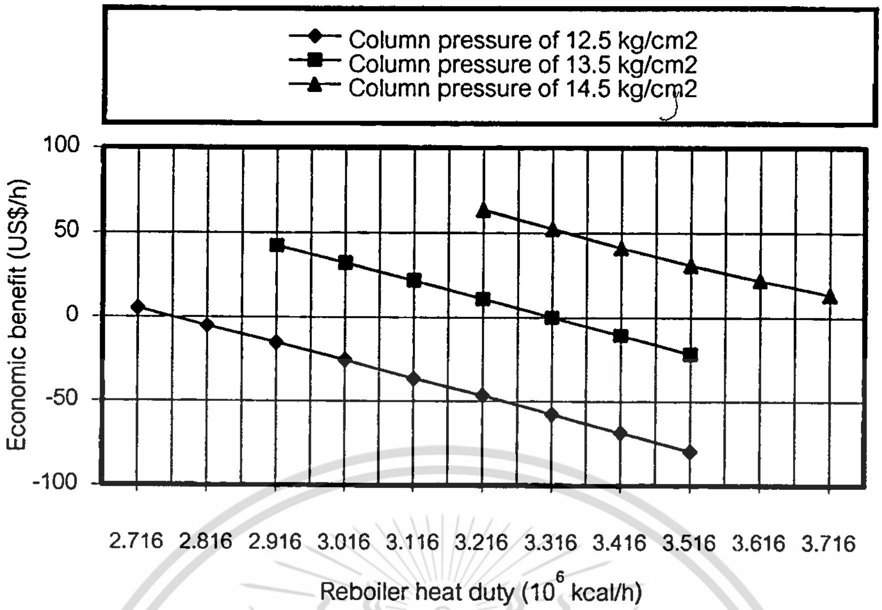


Figure 5.13 The reboiler heat duty and the economic benefit at different column pressures

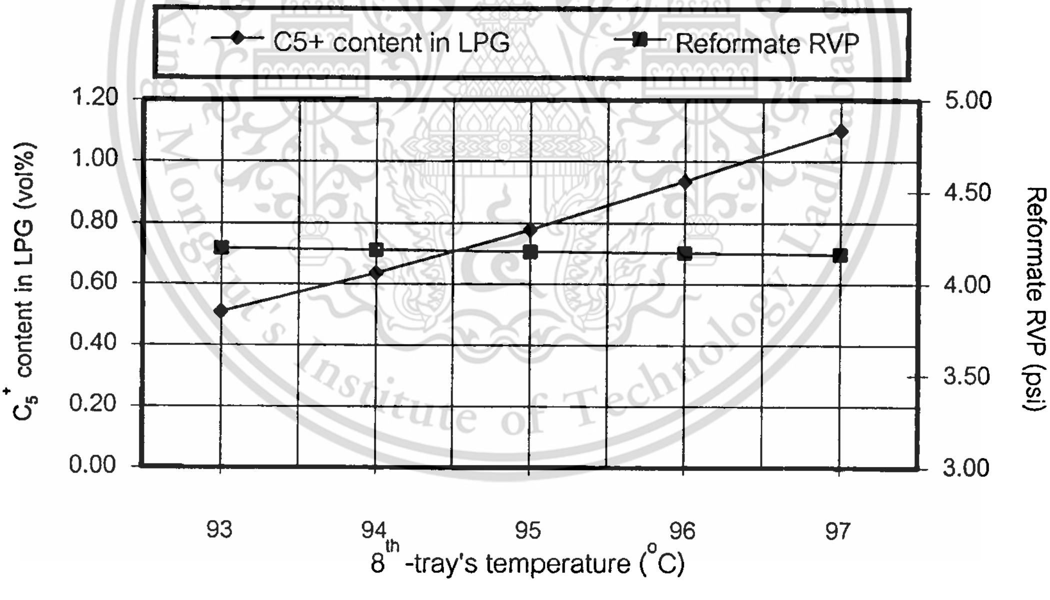


Figure 5.14 Effect of 8th-tray's temperature on C_5^+ content in LPG and reformate RVP

Chapter 6

Conclusions

This work presents an application of simulation as a tool for modeling and optimization of the existing debutanizer in the platforming unit of a petroleum refinery plant to maximize the product yields and the net economic benefit for the most profit within product quality constraints. The studied parameters are column pressure and reboiler heat duty. The simulation results suggest that an increase in economic benefit is observed when column pressure is increased up to 15.5 kg/cm^2,and reboiler heat duty ranges from 2.7163 x10^6 - 3.7163 x10^6 kcal/h. In case of the effect of column pressure at constant reformate RVP at 4.22 psi, it is found that an increase in column pressure up to 15.5 kg/cm^2 leads to an increase in LPG flowrate and fuel gas consumption but does not affect reformate flowrate significantly. This case results in a slight increase in economic benefit so it is not of economic interest.

The effect of reboiler heat duty on the economic benefit is not significant as observed in the case of column pressure at constant reboiler heat duty by controlling reformate RVP within specification range or in other words, "the relaxed reformate RVP case". From the simulation results, to achieve high economic benefit, an increase in column pressure at constant reboiler heat duty (the relaxed RVP case) is preferable. The recommended parameters to obtain the greatest economic benefit of about 61.12 US$/h at the maximum reformate RVP of 5.22 psi are at a column pressure of 14.5 kg/cm^2 and reboiler heat duty of 3.2364 x10^6 kcal/h. Though the approach from this study may not accurately estimate the economic benefit, it however provides valuable information on how the existing debutanizer can be improved and what to expect roughly from such an improvement.

The base model of this work is very useful not only for optimization of the existing debutanizer, but also for debottlenecking, identifying equipment malfunctions, solving product specifications and a guideline to train the operating personnel. In addition, it leads to further studies broadly such as the simulation of other unit processes in the platforming unit or in this refinery plant or others.

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Appendices

Appendix A

Sample of calculation: Economic benefit

As mentioned in Chapter 4, the objective functions of the optimization consist of two major items. The first is to decrease the operating costs associated with fuel cost. The second is the change in the product values of the reformate, LPG, and off gas. Benefit is calculated based on all the product values, of which reformate, LPG, and off gas. The benefit of each case is compared with the base case. The optimal operating conditions that give the highest economic benefit will be selected from the optimization results.

Example: Economic benefit evaluation of a constant reformate RVP case of 4.21 psi: as of the average price in 2003.

Benefit (a base case: 13.5 kg/cm^2) = {(Reformate flowrate x Reformate price) + (LPG flowrate x LPG price) + (Off gas flowrate x Off gas price)} – {Fuel gas flowrate x Fuel gas price}

= {(67.14 x 236.97) + (3.41 x 220.61) + (2.73 x 158)} – {0.38 x 158}

= 17,034.89 US$/h

And that at a constant reformate RVP of 4.21 psi (at column pressure of 14.5 kg/cm^2)

Benefit (14.5 kg/cm^2) = {(67.17 x 236.97) + (3.53 x 220.61) + (2.59 x 158)} – {0.41x 158}

= 17,039.21 US$/h

therefore,

Economic benefit (14.5 kg/cm^2) = Benefit (any case) – Benefit (a base case)

= Benefit (14.5 kg/cm^2) – Benefit (13.5 kg/cm^2)

= 17,039.21 – 17,034.89 US$/h

= 4.32 US$/h

The calculations for other conditions are shown in Table A.2

Table A.1 Sale price of products and cost of energy (as of the average price in 2003)

Reformate (US$/t)	236.97
LPG (US$/t)	220.61
Off gas (US$/t)	158
Fuel gas for reboiler (US$/t)	158

Table A.2 Examples of economic benefit at constant reformate RVP of 4.21 psi

Column pressure (kg/cm^2)	Reformate flowrate (t/h)	LPG flowrate (t/h)	Off gas flowrate (t/h)	Energy consumption or Fuel gas flowrate (t/h)	Product value (US$/h)			Total product value (US$/h)	Energy consumption cost (US$/h)	Benefit (US$/h)	Economic benefit (US$/h)
					Reformate	LPG	Off gas				
11.5	67.08	3.19	3.01	0.32	15,896.27	703.61	475.80	17,075.69	50.07	17,025.62	-9.27
12.5	67.10	3.30	2.88	0.35	15,901.16	728.97	454.38	17,084.51	54.6	17,029.92	-4.98
13.5	67.14	3.41	2.73	0.38	15,909.72	753.25	431.29	17,094.25	59.36	17,034.89	0.00
14.5	67.17	3.53	2.59	0.41	15,916.22	779.06	408.47	17,103.75	64.54	17,039.21	4.32
15.5	67.20	3.64	2.44	0.44	15,924.97	803.77	384.94	17,113.67	69.98	17,043.70	8.80

According to the preliminary economic benefit evaluation by the optimization at the debutanizer column pressure of 14.5 kg/cm^2 and reboiler heat duty of 3.2364 x10^6 kcal/h at the maximum refromate RVP of 5.22 psi, the greatest economic benefit is calculated as shown in Table A.3

Table A.3 The economic benefit at a column pressure of 14.5 kg/cm^2 and reformate RVP of 5.22 psi

Reformate RVP (psi)		Economic benefit (US$/h)
4.9663	3.3163	52.35277
5.2200	3.2364	61.12082
5.2852	3.2163	63.37418

Table A.4 shows the order of tray number of the existing debutanizer (actual) and that used in the simulation model (the simulated tray number)

Table A.4 Comparison of the actual tray number with the simulated tray number of the a base case

	Actual tray number	Simulated tray number
Condenser	32nd tray	1st tray
Temperature control (reflux)	22nd tray	8th tray
Feed tray	10th tray	17th tray
Reboiler	1st tray	25th tray

Appendix B

Input files and summary report of a base case

```
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  PRINT STREAM=ALL, RATE=LV
  DIMENSION METRIC, STDTEMP=0, STDPRES=1.03323
  SEQUENCE SIMSCI
  CALCULATION RVPBASIS=APIN, TVP=37.778
COMPONENT DATA
  LIBID 1,H2/2,1P/3,2P/4,3P/5,4P/6,4P1/7,5P/8,5P1/9,1BUTENE/ &
      10,C2BUTENE/11,T2BUTENE/12,HEXANE/13,IBUTENE/14,PROPENE/ &
      15,3O, SHLB=NONE
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  PROPERTY STREAM=FEEDY, TEMPERATURE=42.04, PRESSURE=16.2, PHASE=M, &
       RATE(WT)=1000, COMPOSITION(M)=4,1.8/5,21.6/6,11.5/7,0.42/ &
      8,0.05, NORMALIZE
  PROPERTY STREAM=FEEDX, TEMPERATURE=44.24, PRESSURE=16.2, PHASE=M, &
       RATE(WT)=67204.4, ASSAY=LV
   D86 STREAM=FEEDX, DATA=0,41.9/5,73.5/10,82.9/20,98/30,111.3/ &
      40,121.5/50,130.1/60,137.5/70,145.1/80,153/90,163.1/95,172.1/ &
      100,209.4, TEMP=C
   SPGR STREAM=FEEDX, AVERAGE=0.8144
  PROPERTY STREAM=OFFGAS, TEMPERATURE=39.18, PRESSURE=13.54, &
       REFSTREAM=FEED2, RATE(WT)=2663.5
  PROPERTY STREAM=REFORMATE, TEMPERATURE=220.4, PRESSURE=13.88, &
       REFSTREAM=SIM-REFORMAT, RATE(WT)=67204.4
  PROPERTY STREAM=LPG, TEMPERATURE=39.38, PRESSURE=13.54, &
       REFSTREAM=FEED3, RATE(WT)=3414.4
  PROPERTY STREAM=FEED1, REFSTREAM=SIM-REFORMAT, RATE(WT)=67204.4
UNIT OPERATIONS
  MIXER UID=M2
    FEED FEEDX,FEEDY
    PRODUCT  M=SIM-REFORMAT
    METHOD SET=SRK01
  CONTROLLER UID=CN1
    SPEC STREAM=SIM-REFORMAT, RVP(D519), VALUE=4.28
    VARY STREAM=FEEDY, RATE(KGM/H)
    CPARAMETER RETURNUNIT=M2, IPRINT, STOP
```

```
 MIXER UID=M1
   FEED FEED3,FEED2,FEED1
   PRODUCT  M=MIX
 HX   UID=E1
   COLD FEED=MIX, M=S1
   OPER CTEMP=154.48
 COLUMN UID=DEBUTANIZER, NAME=07C111
   PARAMETER TRAY=25,IO
   FEED S1,17,SEPARATE
   PRODUCT  OVHD(WT)=OFFGAS,2663.5, BTMS(WT)=REFORMATE,67204.1, &
          LDRAW(WT)=LPG,1,3414.38, SUPERSEDE=ON
   CONDENSER TYPE=MIX, PRESSURE=13.54, TEST=39.61
   DUTY 1,1/2,25
   PSPEC PTOP=13.54, DPCOLUMN=0.311
   PRINT PROPTABLE=PART
   ESTIMATE MODEL=SIMPLE, RRATIO=3.82, CTEMP=39.61, TTEMP=65.91, &
          BTEMP=220.4, RTEMP=245
   TEMPERATURE 1,39.61/2,65.91/8,95/22,173.8/24,220.4/25,245
   SPEC STREAM=REFORMATE, RVP(D519), VALUE=4.28
   SPEC TRAY=2, TEMPERATURE(C), VALUE=65.92
   VARY DUTY=2,1
   REBOILER TYPE=KETTLE
   METHOD SET=SRK01
 CALCULATOR UID=CA1
   DEFINE P(1) AS  COLUMN=DEBUTANIZER, REFLUX(LV,M3/H)
   PROCEDURE
    R(1)=0
    RETURN
END
```

```
SIMULATION SCIENCES INC.          R                    PAGE H-1
PROJECT                  PRO/II  VERSION 5.6 SHELL            386/EM
PROBLEM                        CALCULATION
                         HISTORY                08/24/02

==============================================================================

*** PROBLEM SOLUTION BEGINS
   FEED FLASH    COMPLETE
   UNIT    4    SOLVED   - 'M2         '
    CONTROLLER AT ITERATION    1
      SPECIFICATION MET ... VARIABLE NOT CHANGED
      SPECIFICATION VALUE =  4.28000E+00,  CALC =  4.27845E+00
   UNIT    5    SOLVED   - 'CN1        '
   UNIT    1    SOLVED   - 'M1         '
   UNIT    2    SOLVED   - 'E1         '
        INNER  0 : E(ENTH+SPEC) = 1.968E-04
        RETRIEVING PREVIOUS MATRIX
```

```
      INNER  1 : E(ENTH+SPEC) = 3.899E-06  ALPHA =  1.0000
    ITER  1 E(K) = 2.261E-04 E(ENTH+SPEC) = 3.899E-06  E(SUM) = 5.088E-04
   UNIT    3    SOLVED   - 'DEBUTANIZER '
   UNIT    6    SOLVED   - 'CA1        '
*** PROBLEM SOLUTION REACHED
*** THIS RUN USED 282.92 PRO/II SIMULATION UNITS
*** RUN STATISTICS
   STARTED    20:18:28 09/21/03         NO ERRORS
   FINISHED   20:18:29 09/21/03         NO WARNINGS
   RUN TIMES                          NO MESSAGES
    INTERACTIVE     0 MIN,  0.00 SEC
    CALCULATIONS    0 MIN,  0.78 SEC
    TOTAL           0 MIN,  0.78 SEC
SIMULATION SCIENCES INC.          R                      PAGE I-1
PROJECT                   PRO/II  VERSION 5.6 SHELL          386/EM
PROBLEM                           OUTPUT
                          INDEX               08/24/02

==============================================================================
 PAGE    CONTENTS
------  -----------------------------------------------------
   1   COMPONENT DATA
   4   CALCULATION SEQUENCE AND RECYCLES
   5   MIXER SUMMARY
       HEAT EXCHANGER SUMMARY
   6   UNIT 2, 'E1'
       CALCULATOR SUMMARY
   7   UNIT 6, 'CA1'
       COLUMN SUMMARY
   8   UNIT 3, 'DEBUTANIZER', '07C111'
  10   TRAY RATES AND DENSITIES

SIMULATION SCIENCES INC.          R                      PAGE P-1
PROJECT                   PRO/II  VERSION 5.6 SHELL          386/EM
PROBLEM                           OUTPUT
                       COMPONENT DATA             08/24/02

==============================================================================
    COMPONENT        COMP. TYPE     PHASE    MOL. WEIGHT    DENSITY
                                    KG/M3

  ----------------  ----------  ----------  ----------  ----------

   1  H2                LIBRARY     VAP/LIQ       2.016         69.931
   2  1P                LIBRARY     VAP/LIQ      16.043        299.704
   3  2P                LIBRARY     VAP/LIQ      30.070        356.049
   4  3P                LIBRARY     VAP/LIQ      44.097        507.199
   5  4P                LIBRARY     VAP/LIQ      58.124        583.824
   6  4P1               LIBRARY     VAP/LIQ      58.124        562.545
   7  5P                LIBRARY     VAP/LIQ      72.151        630.378
```

```
  8  5P1                LIBRARY      VAP/LIQ      72.151       622.112
  9  1BUTENE            LIBRARY      VAP/LIQ      56.108       600.707
 10  C2BUTENE           LIBRARY      VAP/LIQ      56.108       626.482
 11  T2BUTENE           LIBRARY      VAP/LIQ      56.108       609.399
 12  HEXANE             LIBRARY      VAP/LIQ      86.178       663.345
 13  IBUTENE            LIBRARY      VAP/LIQ      56.108       599.808
 14  PROPENE            LIBRARY      VAP/LIQ      42.081       521.485
 15  3O                 LIBRARY      VAP/LIQ      42.081       521.485
 16  NBP   21           ASSAY CUT    VAP/LIQ      60.424       737.706
 17  NBP   29           ASSAY CUT    VAP/LIQ      63.486       744.141
 18  NBP   38           ASSAY CUT    VAP/LIQ      67.121       751.470
 19  NBP   52           ASSAY CUT    VAP/LIQ      73.105       762.875
 20  NBP   60           ASSAY CUT    VAP/LIQ      76.313       768.687
 21  NBP   67           ASSAY CUT    VAP/LIQ      79.483       774.240
 22  NBP   80           ASSAY CUT    VAP/LIQ      85.065       783.600
 23  NBP   87           ASSAY CUT    VAP/LIQ      88.499       789.089
 24  NBP   95           ASSAY CUT    VAP/LIQ      92.148       794.522
 25  NBP  102           ASSAY CUT    VAP/LIQ      95.881       799.868
 26  NBP  110           ASSAY CUT    VAP/LIQ      99.711       805.144
 27  NBP  117           ASSAY CUT    VAP/LIQ     103.639       810.346
 28  NBP  125           ASSAY CUT    VAP/LIQ     107.302       815.532
 29  NBP  132           ASSAY CUT    VAP/LIQ     111.036       820.656
 30  NBP  140           ASSAY CUT    VAP/LIQ     114.716       825.538
 31  NBP  147           ASSAY CUT    VAP/LIQ     118.672       830.607
 32  NBP  154           ASSAY CUT    VAP/LIQ     122.468       835.309
 33  NBP  162           ASSAY CUT    VAP/LIQ     126.596       840.250
 34  NBP  170           ASSAY CUT    VAP/LIQ     131.136       845.490
 35  NBP  176           ASSAY CUT    VAP/LIQ     134.378       849.113
 36  NBP  183           ASSAY CUT    VAP/LIQ     138.451       853.533
 37  NBP  190           ASSAY CUT    VAP/LIQ     142.629       857.921
 38  NBP  198           ASSAY CUT    VAP/LIQ     147.655       863.017
 39  NBP  205           ASSAY CUT    VAP/LIQ     151.442       866.731

SIMULATION SCIENCES INC.          R                PAGE P-2
PROJECT                  PRO/II  VERSION 5.6 SHELL        386/EM
PROBLEM                       OUTPUT
                        COMPONENT DATA             08/24/02

==============================================================================
    COMPONENT            NBP    CRIT. TEMP.  CRIT. PRES.  CRIT. VOLM.
                          C          C         KG/CM2     M3/KG-MOL
    -------------     --------   --------    --------    --------

  1 H2                -252.800   -239.900     13.225      0.0650
  2 1P                -161.490    -82.600     46.908      0.0990
  3 2P                 -88.630     32.300     49.802      0.1480
  4 3P                 -42.070     96.670     43.334      0.2030
  5 4P                  -0.500    152.000     38.746      0.2550
  6 4P1                -11.730    134.980     37.196      0.2630
```

```
  7 5P               36.074     196.500     34.355      0.3040
  8 5P1              27.850     187.240     34.479      0.3060
  9 1BUTENE          -6.300     146.400     41.019      0.2400
 10  C2BUTENE         3.700     162.400     42.879      0.2340
 11  T2BUTENE         0.900     155.500     40.606      0.2380
 12  HEXANE          68.740     234.200     30.274      0.3700
 13  IBUTENE         -6.900     144.730     40.792      0.2390
 14  PROPENE        -47.700      91.800     47.115      0.1810
 15  3O             -47.700      91.800     47.115      0.1810
 16  NBP   21        21.612     204.652     49.660      0.2429
 17  NBP   29        29.394     214.228     47.932      0.2532
 18  NBP   38        38.422     225.232     46.103      0.2653
 19  NBP   52        52.824     242.575     43.508      0.2852
 20  NBP   60        60.331     251.519     42.287      0.2958
 21  NBP   67        67.610     260.134     41.176      0.3062
 22  NBP   80        80.119     274.810     39.414      0.3244
 23  NBP   87        87.595     283.506     38.437      0.3355
 24  NBP   95        95.098     292.180     37.508      0.3468
 25  NBP  102       102.582     300.778     36.628      0.3582
 26  NBP  110       110.065     309.323     35.789      0.3698
 27  NBP  117       117.542     317.807     34.990      0.3815
 28  NBP  125       125.091     326.323     34.218      0.3934
 29  NBP  132       132.645     334.791     33.478      0.4055
 30  NBP  140       139.930     342.909     32.793      0.4174
 31  NBP  147       147.586     351.390     32.102      0.4300
 32  NBP  154       154.772     359.302     31.477      0.4420
 33  NBP  162       162.410     367.662     30.838      0.4549
 34  NBP  170       170.610     376.581     30.177      0.4689
 35  NBP  176       176.340     382.779     29.730      0.4788
 36  NBP  183       183.394     390.371     29.195      0.4911
 37  NBP  190       190.473     397.947     28.676      0.5036
 38  NBP  198       198.783     406.788     28.086      0.5185
 39  NBP  205       204.902     413.262     27.665      0.5296

SIMULATION SCIENCES INC.          R                    PAGE P-3
PROJECT                  PRO/II  VERSION 5.6 SHELL          386/EM
PROBLEM                           OUTPUT
                        COMPONENT DATA               08/24/02

==================================================================
    COMPONENT          ACEN. FACT.    HEAT FORM.       G FORM.
                                      KCAL/KG-MOL    KCAL/KG-MOL

    ----------------    ----------    ----------     ----------
  1 H2                   -0.22000          0.00           0.00
  2 1P                    0.01040     -17814.56      -12070.08
  3 2P                    0.09860     -20066.78       -7672.47
  4 3P                    0.15290     -24805.58       -5633.13
  5 4P                    0.20130     -30040.13       -3982.90
```

```
   6  4P1                    0.17720      -32150.09          -5067.47
   7  5P                     0.25060      -34982.56          -2040.48
   8  5P1                    0.22900      -36895.24          -3540.29
   9  1BUTENE                0.19100         -26.80          17030.09
  10  C2BUTENE               0.20219       -1670.01          15712.29
  11  T2BUTENE               0.21860       -2670.01          15022.36
  12  HEXANE                 0.29430      -39872.93            -19.11
  13  IBUTENE                0.19590       -4033.68          13877.76
  14  PROPENE                0.14350        4707.65          14844.27
  15  3O                     0.14350        4707.65          14844.27
  16  NBP   21               0.15876       -3950.41          MISSING
  17  NBP   29               0.16666       -5201.79          MISSING
  18  NBP   38               0.17631       -6660.92          MISSING
  19  NBP   52               0.19256      -22219.42          MISSING
  20  NBP   60               0.20139      -24714.89          MISSING
  21  NBP   67               0.21014      -27192.41          MISSING
  22  NBP   80               0.22560      -26233.85          MISSING
  23  NBP   87               0.23507      -25709.39          MISSING
  24  NBP   95               0.24472      -25093.26          MISSING
  25  NBP  102               0.25450      -24386.18          MISSING
  26  NBP  110               0.26443      -23584.18          MISSING
  27  NBP  117               0.27450      -22685.54          MISSING
  28  NBP  125               0.28481      -21677.11          MISSING
  29  NBP  132               0.29527      -20564.42          MISSING
  30  NBP  140               0.30550      -19391.15          MISSING
  31  NBP  147               0.31640      -18050.32          MISSING
  32  NBP  154               0.32677      -16689.75          MISSING
  33  NBP  162               0.33795      -15133.57          MISSING
  34  NBP  170               0.35013      -13334.70          MISSING
  35  NBP  176               0.35875      -11998.02          MISSING
  36  NBP  183               0.36949      -10260.93          MISSING
  37  NBP  190               0.38040       -8415.64          MISSING
  38  NBP  198               0.39340       -6794.84          MISSING
  39  NBP  205               0.40310       -8154.10          MISSING

SIMULATION SCIENCES INC.         R                      PAGE P-4
PROJECT                PRO/II  VERSION 5.6 SHELL            386/EM
PROBLEM                          OUTPUT
                  CALCULATION SEQUENCE AND RECYCLES           08/24/02

==============================================================================
CALCULATION SEQUENCE
 SEQ  UNIT ID     UNIT TYPE     SEQ   UNIT ID     UNIT TYPE
  ---  -----------    ---------     ---   -----------    ---------

  1  M2             MIXER         4  E1              HX
  2  CN1          CONTROLLER      5              DEBUTANIZER   COLUMN
  3  M1             MIXER         6  CA1          CALCULATOR
```

```
SIMULATION SCIENCES INC.        R                    PAGE P-5
PROJECT               PRO/II  VERSION 5.6 SHELL          386/EM
PROBLEM                      OUTPUT
                     MIXER SUMMARY               08/24/02

==============================================================================
MIXER ID                  M1        M2
   NAME
   FEEDS                FEED3     FEEDX
                        FEED2     FEEDY
                        FEED1
                            PRODUCTS MIXED          MIX
                               LIQUID           SIM-REFORMAT

TEMPERATURE, C                  50.140            44.285
PRESSURE, KG/CM2                16.200            16.200
PRESSURE DROP, KG/CM2            0.000             0.000
MOLE FRAC VAPOR                  0.01683           0.00000
MOLE FRAC LIQUID                 0.98317           1.00000

SIMULATION SCIENCES INC.        R                    PAGE P-6
PROJECT               PRO/II  VERSION 5.6 SHELL          386/EM
PROBLEM                      OUTPUT
                   HEAT EXCHANGER SUMMARY               08/24/02

==============================================================================
                   UNIT 2, 'E1'
OPERATING CONDITIONS
  DUTY, M*KCAL/HR                 4.200

COLD SIDE CONDITIONS                INLET      OUTLET
                                  ---------  ---------
  FEED                                  MIX
  MIXED,PRODUCT                                   S1
   VAPOR, KG-MOL/HR                 13.500     65.736
        K*KG/HR                      0.158      3.119
     CP, KCAL/KG-C                   0.827      0.543
  LIQUID, KG-MOL/HR                788.622    736.386
        K*KG/HR                     73.124     70.163
     CP, KCAL/KG-C                   0.467      0.583
   TOTAL, KG-MOL/HR                802.122    802.122
        K*KG/HR                     73.282     73.282
  VAPORIZATION, KG-MOL/HR                      52.236
   TEMPERATURE, C                   50.140    154.480
   PRESSURE, KG/CM2                 16.200     16.200

SIMULATION SCIENCES INC.        R                    PAGE P-7
PROJECT               PRO/II  VERSION 5.6 SHELL          386/EM
```

```
PROBLEM                    OUTPUT
                   CALCULATOR SUMMARY          08/24/02

=====================================================================
                 UNIT 6, 'CA1'
  RESULT     NAME      VALUE        RESULT    NAME       VALUE
  -------   --------   --------     ------   --------   --------

     1          0.00000E+00    2- 200           UNDEFINED
SIMULATION SCIENCES INC.         R                PAGE P-8
PROJECT                 PRO/II  VERSION 5.6 SHELL        386/EM
PROBLEM                    OUTPUT
                    COLUMN SUMMARY           08/24/02

=====================================================================
              UNIT 3, 'DEBUTANIZER', '07C111'
TOTAL NUMBER OF ITERATIONS
  IN/OUT METHOD     25
COLUMN SUMMARY
                ---------- NET FLOW RATES -----------    HEATER
 TRAY   TEMP     PRESSURE      LIQUID       VAPOR   FEED       PRODUCT      DUTIES
        DEG C     KG/CM2                      KG-MOL/HR
M*KCAL/HR
 ----- ------ -------- -------- ------- -------- -------- ----------

  1C    32.0      13.54        186.2                               76.9V       -1.1650
                                                                   66.4L

  2     60.57     13.54        201.4         329.5
  3     66.2      13.55        198.4         344.7
  4     73.4      13.57        193.1         341.7
  5     82.8      13.58        187.2         336.4
  6     84.0      13.59        181.5         330.5
  7     89.1      13.61        176.4         324.8
  8     94.9      13.62        171.8         319.7
  9     96.8      13.63        167.5         315.1
 10     98.5      13.65        163.1         310.8
 11    101.4      13.66        158.0         306.4
 12    103.6      13.68        151.7         301.3
 13    105.7      13.69        143.5         295.0
 14    111.1      13.70        131.8         286.8
 15    119.1      13.72        112.5         275.1
 16    132.9      13.73         84.8         255.8     87.9V
 17    157.2      13.74        861.9         140.2    714.2L
 18    160.2      13.76        888.1         203.1
 19    162.4      13.77        906.2         229.3
 20    164.7      13.78        922.3         247.3
 21    167.8      13.80        939.5         263.4
 22    173.5      13.81        961.6         280.6
 23    180.7      13.82        993.5         302.8
 24    194.9      13.84       1036.2         334.7
 25R  218.6       13.85        377.4         658.8L                                3.3163
```

```
 FEED AND PRODUCT STREAMS
  TYPE   STREAM          PHASE         FROM  TO    LIQUID     FLOW RATES   HEAT
RATES
                                       TRAY TRAY    FRAC       KG-MOL/HR

M*KCAL/HR
 ----   ----------    -----   ---  ---     -----     ----------     ----------
  FEED       S1             MIXED                 17    0.8904         802.12
5.8218
  PROD       OFFGAS         VAPOR        1                               76.94
0.2811
  PROD       LPG            LIQUID       1                               66.36
0.0778
  PROD       REFORMATE    LIQUID       25                               658.82
7.6144
  OVERALL MOLE BALANCE, (FEEDS - PRODUCTS)          -2.9976E-13
  OVERALL HEAT BALANCE, (H(IN) - H(OUT)  )              -6.1959E-06
 SIMULATION SCIENCES INC.          R                 PAGE P-9
 PROJECT                  PRO/II  VERSION 5.6 SHELL          386/EM
 PROBLEM                               OUTPUT
                         COLUMN SUMMARY                08/24/02

 ==============================================================================
               UNIT 3, 'DEBUTANIZER', '07C111'  (CONT)
 SPECIFICATIONS

    PARAMETER            TRAY   COMP      SPECIFICATION       SPECIFIED
CALCULATED
     TYPE                  NO      NO             TYPE               VALUE          VALUE
    --------------         ----    -----      -----------         ---------       ---------
  STRM REFORMATE      25                      RVP             4.280E+00      4.280E+00
  TRAY LIQ                 2               TEMPERATURE        6.592E+01      6.592E+01
  STRM LPG                 1      1- 39        WT  RATE          3.414E+03      3.414E+03

 SIMULATION SCIENCES INC.          R                 PAGE P-10
 PROJECT                  PRO/II  VERSION 5.6 SHELL          386/EM
 PROBLEM                               OUTPUT
                         COLUMN SUMMARY                08/24/02

 ==============================================================================
               UNIT 3, 'DEBUTANIZER', '07C111'  (CONT)
 TRAY NET VAPOR RATES AND DENSITIES
                                                          -------------- RATES --------------
  TRAY     MW     ACTUAL DENS       Z FROM                        NORMAL       ACTUAL
                      KG/M3          DENSITY        K*KG/HR     K*M3/HR      K*M3/HR
   ----    -------    ----------          -------         ---------      ---------      ---------
   1     35.479     20.58737          0.88002          2.730        1.724          0.133
   2     47.720     27.48177          0.81785         15.723        7.385          0.572
   3     49.798     28.26976          0.81312         17.167        7.727          0.607
   4     50.550     28.34146          0.81422         17.272        7.659          0.609
   5     50.935     28.21742          0.81687         17.132        7.539          0.607
```

```
  6    51.212    28.03630         0.81999     16.925     7.408      0.604
  7    51.463    27.85505         0.82305     16.716     7.281      0.600
  8    51.712    27.69806         0.82581     16.532     7.165      0.597
  9    51.965    27.56942         0.82823     16.375     7.063      0.594
 10    52.228    27.45988         0.83045     16.234     6.967      0.591
 11    52.516    27.35351         0.83272     16.091     6.867      0.588
 12    52.858    27.23275         0.83533     15.925     6.753      0.585
 13    53.285    27.07895         0.83858     15.718     6.612      0.580
 14    53.835    26.85840         0.84298     15.440     6.428      0.575
 15    54.541    26.46221         0.85001     15.003     6.165      0.567
 16    55.455    25.62072         0.86315     14.184     5.733      0.554
 17    60.612    26.42859         0.86378      8.497     3.142      0.321
 18    63.371    27.84843         0.85209     12.869     4.552      0.462
 19    64.989    28.64931         0.84584     14.901     5.139      0.520
 20    66.312    29.26636         0.84119     16.402     5.544      0.560
 21    67.652    29.82337         0.83718     17.822     5.905      0.598
 22    69.374    30.43567         0.83306     19.470     6.290      0.640
 23    72.091    31.28889         0.82773     21.830     6.787      0.698
 24    76.840    32.70212         0.81941     25.717     7.501      0.786
 25    85.506    35.25691         0.80517     32.266     8.458      0.915

SIMULATION SCIENCES INC.        R               PAGE P-11
PROJECT              PRO/II  VERSION 5.6 SHELL       386/EM
PROBLEM                    OUTPUT
                     COLUMN SUMMARY              08/24/02

=====================================================================
           UNIT 3, 'DEBUTANIZER', '07C111'  (CONT)
TRAY NET LIQUID RATES AND DENSITIES

                                                   ---------- RATES ----------
TRAY       MW      ACTUAL DENS   Z FROM                  STD LIQ    ACTUAL
                     KG/M3       DENSITY      K*KG/HR     M3/HR      M3/HR
----     -------   ----------   -------     ---------  ---------  ---------
  1      51.450     512.051     0.05131        9.579     17.574     18.707
  2      54.724     498.301     0.05172       11.023     19.356     22.120
  3      56.094     503.851     0.05139       11.128     19.057     22.087
  4      56.918     512.000     0.05075       10.988     18.416     21.461
  5      57.593     521.360     0.04999       10.781     17.690     20.679
  6      58.242     531.036     0.04923       10.572     16.989     19.909
  7      58.891     540.165     0.04857       10.388     16.371     19.230
  8      59.546     548.158     0.04805       10.231     15.851     18.664
  9      60.227     554.888     0.04769       10.090     15.407     18.183
 10      60.987     560.650     0.04750        9.946     14.997     17.741
 11      61.912     565.970     0.04745        9.781     14.574     17.282
 12      63.120     571.421     0.04754        9.574     14.092     16.755
 13      64.778     577.538     0.04780        9.296     13.495     16.096
 14      67.227     585.089     0.04832        8.859     12.646     15.141
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15	71.484	596.235	0.04944	8.040	11.214	13.484
16	80.130	614.814	0.05197	6.794	9.143	11.051
17	92.827	626.906	0.05577	80.007	103.704	127.622
18	92.375	620.663	0.05573	82.040	106.577	132.180
19	92.191	616.870	0.05573	83.540	108.604	135.426
20	92.122	613.926	0.05571	84.960	110.421	138.388
21	92.188	611.383	0.05565	86.608	112.375	141.659
22	92.518	608.838	0.05554	88.968	114.971	146.127
23	93.462	605.647	0.05544	92.855	119.061	153.315
24	95.934	600.797	0.05568	99.404	125.816	165.454
25	101.906	592.777	0.05707	67.138	83.376	113.260

Biography

Name		Panudej Sukkhet
Date of birth		7 June 1969
Place of birth		Phuket, Thailand
Education		Bachelor of Science (Chemistry), Department of Chemistry, Faculty of Science and Industry, King Mongkut's University of Technology Thonburi, 1985 – 1989
Work experiences	-	May, 1989 – June, 1995 at the Thai Petrochemical Industry Co., Ltd.
	-	October, 1995 – August, 2000 at the Star Petroleum Refining Company Ltd.
	-	August, 2000 – present at the Alliance Refining Company Ltd.
Senior project		Title: Quality improvement of high-pour point fuel oil by solvent dewaxing process
Master thesis		Title: Optimization of the debutanizer in a platforming unit using PRO/II
Publications	-	Anchaleeporn W. Lothongkum and P. Sukkhet, "A Case Study of Using Light Cracked Gas Oil in the Diesel Hydrodesulfurization Unit to Estimate the H_2 Consumption and to Optimize the Production in a Refinery Plant." Engineering Journal, Kasertsat University, Thailand, vol. 3, no 39, Dec. 1999 – Jan. 2000 (in Thai).

Biography (cont.)

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