MODELING AND SIMULATION OF CRUDE DISTILLATION UNIT (CDU)

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MODELING AND SIMULATION OF CRUDE DISTILLATION UNIT (CDU)

OH SHU YIN

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
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SUPERVISOR'S DECLARATION

I hereby declare that we have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

Signature :

Name of supervisor : DR RAMESH KANTHASAMY

Position : SENIOR LECTURER

Date : JANUARY 2014

STUDENT'S DECLARATION

I declare that the work in this thesis is my own except for the quotations and summaries which have been duly acknowledged.

Signature :

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Date : JANUARY 2014

DEDICATION

Dedicated to:

My family,

my lecturers,

and my fellow friends

for all their support and help given to me.

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ABSTRACT

There is rapid growth in the usage and demand of crude oil in various industrial fields. Thus, the price of the petrol is rising due to the stronger-than-expected demand for petroleum products. Nowadays, simulation has become an important tool in the behavior study of almost all chemical processes. A proper modeling can bring great advantages to an industry, among them, the increase in knowledge about the process without the need to carry out the real processes. A good model is necessary to develop a proper control strategy for crude distillation unit (CDU) as it can provide more accurate behaviour study of the real system. Due to the lack of proper simulation of CDU, this research is aimed to develop modeling and simulation of CDU. Data of crude oil, the operating conditions of the involved units, and other essential data were collected and entered into the simulation software, Aspen Plus to generate the CDU model. The completed simulation of CDU was run and the results were studied. By solving model equations, the effect of different operating conditions of petroleum refining towards the yield and composition of petroleum products was determined. The higher the feed flow rate, the higher the products feed flow rates. To ensure the simulation is working, the results obtained were compared to previous works done by other researchers and were proven to be valid. Various information about the system under study were obtained easily using the CDU simulation model. The objectives of this research were accomplished.

ABSTRAK

PEMODELAN UNIT PENYULINGAN MINYAK MENTAH

Penggunaan dan permintaan terhadap minyak mentah semakin meningkat dalam pelbagai industri. Justeru, harga petrol turut meningkat disebabkan permintaan yang lebih tinggi daripada penghasilan produk petroleum. Pada masa kini, simulasi telah menjadi suatu alat yang penting bagi mengkaji sistem pelbagai proses kimia. Suatu model yang baik akan membawa kebaikan kepada sesuatu industri, seperti menambahkan ilmu berkaitan suatu proses tanpa menjalankan proses tersebut. Model yang baik diperlukan untuk mengembangkan strategi kawalan yang sesuai untuk unit penyulingan minyak mentah kerana ia dapat memodelkan keadaan sistem yang dikaji dengan lebih tepat. Disebabkan kekurangan model unit penyulingan minyak mentah yang tepat, kajian ini bertujuan untuk menjana model unit penyulingan minyak mentah. Data minyak mentah, keadaan operasi bagi unit yang terlibat dan data penting yang lain telah dikumpulkan dan dimasukkan ke dalam perisian simulasi, Aspen Plus untuk menjana model unit penyulingan minyak mentah. Simulasi yang telah siap telah diuji dan keputusan yang diperoleh telah dianalisi. Dengan menyelesaikan persamaan model, kesan keadaan operasi yang berbeza dalam penapisan petroleum terhadap hasil dan komposisi produk petroleum telah dikaji. Semakin tinggi kadar aliran masuk minyak mentah, semakin tinggi kadar aliran keluar produk petroleum. Bagi memastikan model yang dijana berkesan, keputusan yang diperoleh telah dibandingkan dengan kajian-kajian yang pernah dijalankan oleh penyelidik lain dan telah terbukti sah. Pelbagai maklumat mengenai sistem yang dikaji dapat diperoleh dengan mudah dengan menggunakan model simulasi unit penyulingan minyak mentah ini. Objektif kajian telah tercapai.

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LIST OF ABBREVIATIONS

ADU	Atmospheric distillation unit
AE	Algebraic equations
AGO	Atmospheric gas oil
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
BK10	Braun K10
CDU	Crude distillation unit
CS	Chao-Seader
ENGPETRO	English Engineering units appropriate for Petroleum applications
EOS	Equations of state
H	Enthalpy
HEN	Heat exchanger network
K	Phase equilibrium
MESH	Mass balance, equilibrium, summation and enthalpy balance
ODE	Ordinary differential equation
PA	Pumparound
PC	Pseudocomponent
PID	Proportional Integral Derivative
PR	Peng-Robinson
RKS	Redlich-Kwong-Soave
StdVol	Standard volume
TBP	True boiling point
VDU	Vacuum distillation unit

CHAPTER 1

INTRODUCTION

1.1 Background of Study

A model is a representation of a real object or system of objects for visual or behavior analyzing purposes. Simulation is the transition of a mathematical or computer model to a description of the system behavior based on sets of input parameters (Barr, 2007). Modeling and simulation are important in engineering because description of system behavior by experimentation might not be feasible due to inaccessible inputs and outputs, experiment is too dangerous, very high experimentation cost, experimental behavior might be obscured by disturbances and/or time constants of the system may not be compatible with human dimensions.

There are two types of modeling, namely steady state modeling and dynamic modeling. The models for chemical processes are generally developed for steady state and dynamic modes (Goncalves, Martins, & Feyo de Azevedo, 2010). Steady state models can generally perform steady state material and energy balances, determine different plant scenarios, and optimize capital and equipment costs to obtain best profits, which is very useful in project stage. However, steady state models are of limited use because chemical plants do not operate in steady state. This is where dynamic models come in

vital need. Dynamic models describe the change of system properties over time. Dynamic modeling can provide users a better understanding and operational capabilities of dynamic processes. Therefore, nowadays dynamic simulation has become an essential tool in behavior study of almost every process.

Crude distillation units (CDU) are fractional distillation columns for the distillation of crude oils. A CDU is also known as an atmospheric distillation column (ADU) as it operates at atmospheric pressure. It is the first major unit in refineries for crude oil processing, the central, and the most important unit of all crude oil refineries (Goncalves *et al*., 2010) because distillation is the first step in the processing of crude oil. CDUs are key process plants in petroleum refinery because they produce intermediate streams that are used in downstream process units. In the CDU, crude oil, which is a mixture of many types of hydrocarbons, is boiled and condensed to separate the crude oil into various components such as naphtha, kerosene, diesel and gas oil, based on the boiling points of the respective components. Figure 1-1 shows the basic flow diagram for conventional distillation and associated unit operations. PA in Figure 1-1 stands for pumparound while HEN stands for heat exchanger network.

Changes in CDU have great impact on product yields and quality (Lopez, Mahecha, Hoyos, Acevedo, & Villamizar, 2009). Therefore, CDUs are recommended to be operated at optimal conditions from technical and economical aspects.

Many types of commercial process simulators are available in the market today. In this research, Aspen Plus will be used to develop the steady state CDU simulation.

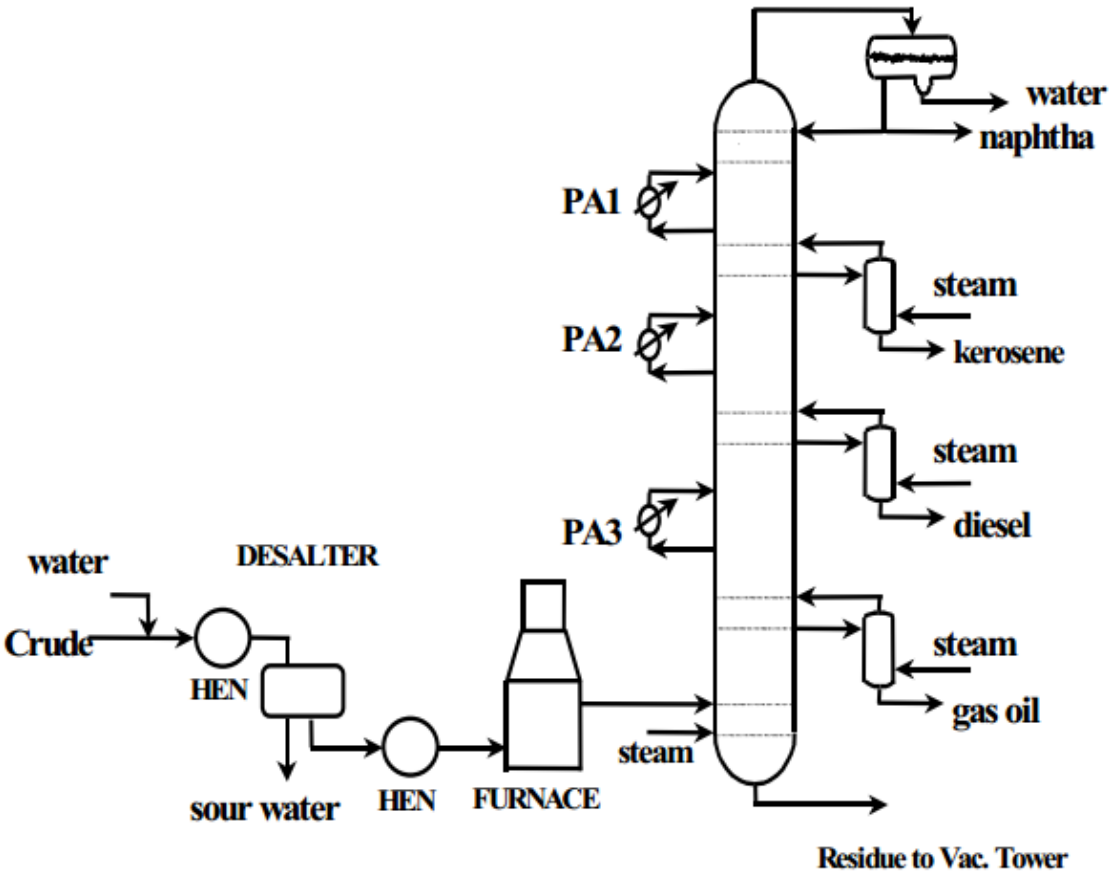

Figure 1-1 Crude Distillation Unit and Associated Unit Operations

Crude oil or petroleum is a complex mixture of carbon and hydrogen, which exist as a liquid in the earth's crust (Ophardt, 2003). Crude oils vary in colour, from clear to tar-black, and in viscosity, from water to almost solid. Crude oils need to be refined before it is further processed into various products for human daily usage such as vehicle petrol and plastic chairs.

In crude oil distillation process, crude oil is desalted in a Desalter and then heated to about 350°C-400°C in a series of heat exchangers before being piped into a CDU. Figure 1-2 shows the fractionation column and trays. In the CDU, the liquid falls to the bottom and the vapor rises, passing through a series of perforated trays called sieve trays. Heavier hydrocarbons condense faster than the lighter ones and will settle on lower trays while lighter hydrocarbons condense on higher trays. The liquid fractions are then drawn out from the unit. Light gases, methane, ethane, propane and butane are collected from the top of the column, petrol is formed in top trays, kerosene and gas oils in the middle, and fuel oils at the bottom (Refining of Petroleum, n.d.). The residue

drawn from the bottom may be processed into lubricants, waxes and bitumen, burned as fuels or used as feedstock for cracking units. Crude oil products obtained after the distillation in the CDU can be further processed into various useful products for human daily life usage, for example, vehicle petrol, chemicals in skincare products and lubricants in factories.

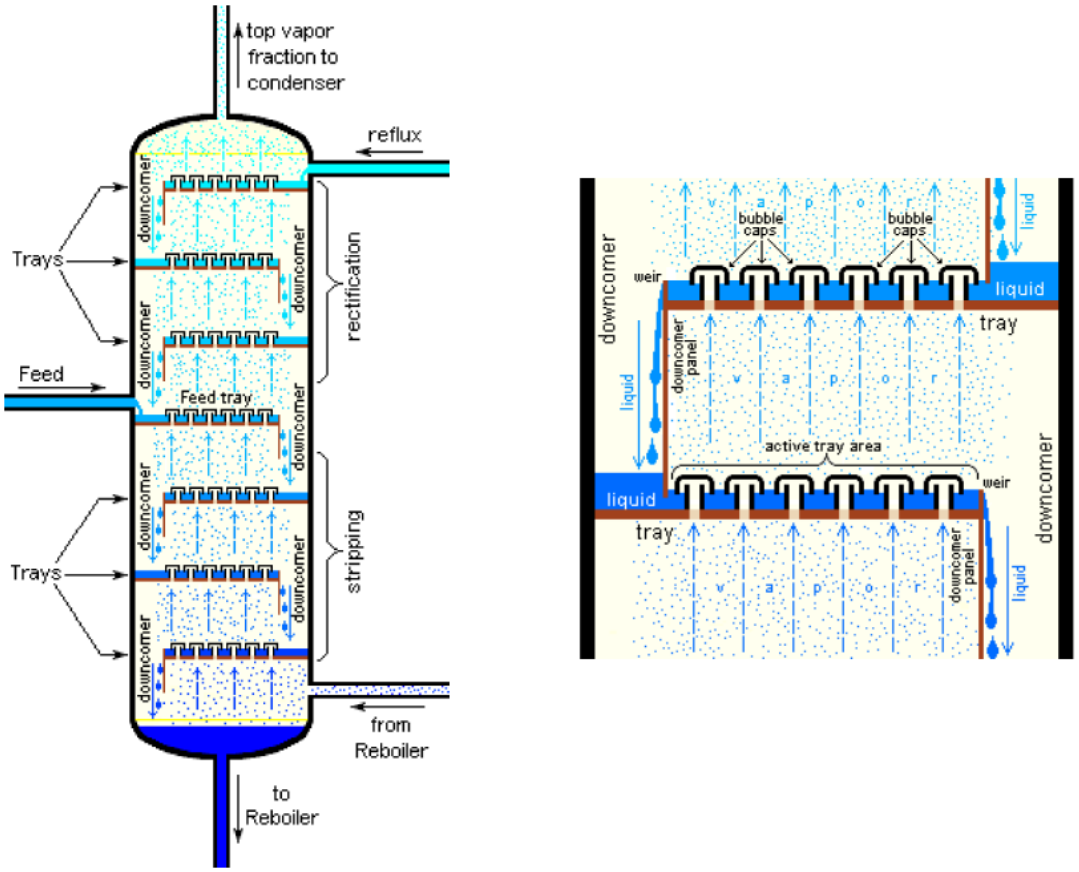

Figure 1-2 Fractionation Column and Trays

1.2 Motivation and Problem Statement

There is rapid growth in the usage and demand of crude oil in various industrial fields such as plastic industry, synthetic rubber industry and pharmaceutical industry. The crude oil refining process should be studied more carefully so as to provide more information to engineers to upgrade or enhance the efficiency of the various equipments required. This is where the dynamic modelling and simulation of CDU comes in useful.

Dynamic models allow us to understand the behavior of the dynamic system of study besides resolving industrial problems or processes that are of immediate and contemporary interest. Although distillation is a widely used unit operation in chemical

process industries, the development of dynamic models continues to be an active research area (Wong & Seborg, n.d.). In crude oil distillation process, when the feed flow rate or feed composition in altered, the product compositions will change as well. According to Radulescu (2007), due to the importance of CDU and its complexity as well as high energy consumption involved, it is very important to have powerful instruments to intimately study it. Since the dynamic modeling of CDU is quite difficult due to process complexity and problems affecting the numerical integration of the model equations, there is no proper dynamic model and simulation of CDU (Radulescu, 2007). A proper dynamic simulation of CDU can provide the people working with this system a wider knowledge about its behavior besides serving as a demonstration during trainings for new engineers in the industry. Therefore, it is necessary to have an accurate dynamic modeling of a CDU in order to have full control over the unit after it is built.

1.3 Research objective

The objectives of this research are:

i) To develop a model of CDU

ii) To study the effect of different operating conditions of petroleum refining toward the yield and composition of petroleum products by solving model equations

1.4 Scope of Study

The scopes of this research have been identified in order to achieve the research objectives. The scopes are:

i) To develop a model of CDU based on the component and overall mass balance, enthalpy balance, and vapor-liquid equilibrium equation by building up a mathematical model for the crude oil refining process

ii) To validate the model by comparing the model results and the data obtained from previous researches done by other researchers

1.5 Main Contribution of This Work

The followings are the contributions that this study could provide:

i) Improve previous researches on dynamic modeling and simulation of CDU

ii) Solve problems faced by crude refining industries

1.6 Thesis Organisation

The structure of the remainder of the thesis is outlined as follow:

Chapter 2 presents the review of previous studies done related to this research. This chapter discusses in detail about the mathematical model for CDU, thermodynamic method which will be chosen, types of mathematical model available, the simulation software which will be used for this study, which is Aspen Plus (for steady state CDU model simulation), the boiling point analysis, as well as the assumptions and simplifications that will be made for this study. A summary of past researches is included in this chapter.

Chapter 3 gives an overview of the simulation environment. This chapter introduces the general procedure in developing a dynamic model, starting from the very first step, which is to define the objectives of the research. Besides that, the steps involved in developing a simulation of CDU model using Aspen Plus are described in this chapter.

Chapter 4 presents the result obtained from the completed simulation of CDU, which are illustrated in the form of graphs and tables. Comparisons of result obtained with past researches are also discussed in this chapter.

Chapter 5 consists of the summary made for this research, together with the recommendation for future research related to this research topic.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

This chapter presents the detailed information and classification of crude oil, as well as the details about the CDU besides describing the importance of modeling and simulation. This chapter also discusses about the mathematical model for CDU in detail. Next, this chapter also reviews the thermodynamic methods, types of mathematical model and the modeling software which are involved in this study. Lastly, this chapter includes the boiling point analysis, the assumptions and simplifications which need to be considered in this study, and the summary of past researches done by other researchers.

2.2 Introduction

Different regions on earth tend to have different types of crude oil, so crude oil is often classified based on where it comes from. Crude oil quality is measured in terms of density and sulfur content. Its density is classified as light, medium or heavy according to its measured American Petroleum Institute (API) gravity. API gravity is a measure of how heavy or how light a petroleum liquid is compared to water at a temperature of

15.6°C (Facts About Crude Oil, 2000). Light crude has API gravity higher than 38°API, medium crude has API gravity between 22.3°API and 31.1°API, and heavy crude has API gravity below 22.3°API. If its API is greater than 10, it is heavier than water and therefore, sinks. Most values fall between 10°API and 70°API. Lighter oils are more valuable than heavy oils because more gasoline can be created from a smaller amount. According to Facts about Crude Oil (2000), crude oil with sulfur content less than 0.5% is commonly defined as sweet crude, while sour crude has sulfur content greater than 0.5%. To extract the maximum value from crude oil, it first needs to be refined into petroleum products.

There are different types of CDU model available for the distillation of crude oil. To achieve a good separation between the different products, the CDU is designed to have 30 or more trays. A CDU can be divided into two sections: rectifying section and stripping section. The rectifying section of the CDU uses heat to separate the components of crude oil based on their volatilities. The temperature of each tray decreases as the vapor proceeds up the CDU, allowing only the more volatile components to continue travelling upwards through the CDU (Brunetti, Howard, & Bagajewicz, n.d.). There is a condenser on top of the column, which condenses the exiting overhead vapor stream. The condensate is parted into two portions: one will be refluxed as a liquid phase that cascades down the column while the other will exit the condensate as distillate. According to Brunetti *et al.* (n.d.), the stripping section is similar to the unit operation of stripping. In conventional distillation model, steam enters the bottom tray in the CDU and rises through the trays below the feed, stripping the lighter components to the rectifying section. The crude oil components are separated by the stripping action of the steam. Besides having strippers, the CDU also consists of pumparounds, which are required to ensure liquid reflux within the column. According to Hovd, Michaelsen & Montin (1997), the upper and lower pumparounds are where liquid is withdrawn from the column and heat exchanged before being returned to the column. These pumparounds and the capacity of the condenser for the top product are important constraints when maximizing throughput and optimizing energy efficiency, but are not used for control of product quality or yield (Hovd *et al*., 1997). In order to recover as much heat as possible from the distilled units, pumparound streams and product streams recover heat in the preheat trains for the column feeds. The complex heat integration schemes and the interactive nature of the process due to the presence of

pumparound and side-stripper distillation features make it difficult to operate at the optimal conditions (Robertson, Palazoglu & Romagnoli, 2011). According to Robertson *et al.* (2011), the decision variables of the operational level are the stripping steam mass flow rates, product flow rates, pumparound flow rates, overhead column flow rates, and atmospheric and vacuum furnace outlet temperatures.

Dynamic models allow us to examine relationships that could not be sorted out by purely experimental methods, and to make forecasts that cannot be made strictly by extrapolating from data (Ellner & Guckenheimer, 2006). Dynamic simulation allows the prediction of dynamic behavior of the process and also assists in evaluation or design of the control strategies (Bezzo, Bernardi, Cresmonese, Finco & Barolo, 2004) besides being an essential prerequisite for a project engineer attempting to design new units or rate existing units (Kumar, Sharma, Chowdhury, Ganguly & Saraf, 2001). Using modeling and simulation software to construct a model for the system of study can save the time by 80% compared to constructing an actual working model, besides saving cost (Guven, n.d.). According to Guven (n.d.), by using a software prototype and testing the model under computerized simulation conditions, it enables users to quickly and easily find out the problem encountered by the model. With computer modeling and simulation, engineers do not need to retest the same part of operation with thousands of different configurations, which would cost thousands of dollars as well as hours to accomplish, because a computer software prototype can be easily used to test it on thousands of different conditions.

2.3 Mathematical Model for CDU

Mathematical model is an abstract model that uses mathematical languages to describe the behavior of a system. Mathematical modeling can be used in many cases, for example, to develop scientific understanding through the quantitative expression of current knowledge of a system, to test the effect of changes in a system, and to aid decision making (An Introduction to Mathematical Modelling, n.d.).

According to Doust, Shahraki & Sadeghi (2012), the appropriate way to solve a problem involving multiple-stage separation for systems in which different phases and different components play their parts, is to resort to simultaneous or iterative solutions of hundreds of equations. It is necessary to specify a sufficient number of design

variables so that the number of unknown quantities, the output variables, is exactly the same as the number of equations, the independent variables (Doust *et al.*, 2012). This set of equations can be found and counted in a mathematical model.

The model equations for an ordinary equilibrium stage of a simple distillation column, namely mass balance, equilibrium, summation and enthalpy balance (MESH), need to be solved first as mathematical modeling is an important part of economic design. These are the fundamental material and energy balance equations which can facilitate numerical stability and ease of convergence (Kumar *et al.*, 2001). For dynamic modeling, the ordinary differential equations (ODE) and algebraic equations (AE) will need to be solved too, as it they are important to show changes within the process with time. According to Kumar *et al.* (2001), from a practical view-point, it is not possible to represent the crude oil feed or its distillation products in terms of actual component flow rates or mole fractions since crude oil is a mixture of several hundred constituents which are not easy to analyze. A general practice is to express the composition of crude oil in terms of a finite number of pseudo-components and each pseudo-component is characterized by an average boiling point and an average specific gravity and is treated as a single component (Kumar *et al.*, 2001).

According to Haydary & Pavlik (2009), theoretical stage method is usually used for mathematical description of a distillation process in refining columns. The real number of stages might need to be multiplied by column efficiency in order to find the number of theoretical stages of an existing column (Doust *et al.*, 2012). The mass balance for individual components or pseudo-components, enthalpy balance, and vapor liquid equilibrium equation can be written for each theoretical stage. The sum of these equations creates the mathematical model of a theoretical stage which in turn makes up the mathematical model of a column.

2.4 Thermodynamic Method

One of the fundamentals to process simulation is to select a suitable thermodynamic model for the prediction of the enthalpy (H) and the phase equilibrium (K) (Edwards, 2008). The appropriate thermodynamic method is the most essential step in developing an accurate simulation without errors. The selection of appropriate thermodynamic model depends on the detailed knowledge of thermodynamics and practical experience.

Guidelines for thermodynamic method selection includes the process species and compositions, pressure and temperature operating ranges, system phases involved, nature of the fluids, and the availability of data (Edwards, 2008). There are four categories of thermodynamic models or four main types of Property Methods and they are Ideal, Equations-of-State (EOS), Activity Coefficient, Empirical and Special System Specific. Petroleum-tuned EOS are used at high pressures. The hydrocarbons can be from natural gas or crude oil, that is, complex mixtures that are treated using pseudo-components.

According to Kumar *et al.* (2001), computation of equilibrium constants of various components present and enthalpies of different streams as the function of temperature and composition are essential for a distillation column simulator. Empirical or semi-empirical correlations are commonly used in estimating these thermodynamic properties (Kumar *et al.*, 2001). The four categories of thermodynamic Property Methods mentioned in the paragraph above are available in Aspen Plus. However, there are only two groups of methods suitable for crude oil refining process. One is based on the EOS of gas while the other is specially developed for hydrocarbon mixture. The state of equation of gases is suitable for real components. Peng-Robinson (PR) and Redlich-Kwong-Soave (RKS) are examples of state equations. The group which is specially developed for hydrocarbon mixture is suitable for pseudo-components. Examples are Braun K10 (BK10) and Chao-Seader (CS). Kumar *et al.* (2001) stated that the thermodynamic properties of vapor-liquid mixtures are usually predicted by calculating deviations from ideality of both the vapor and liquid phases by using any of the EOS. Another method is to apply the EOS only to the vapor state while the liquid phase deviations from ideal behavior are calculated using thermodynamic excess functions.

Doust *et al.* (2012) and Haydary & Pavlik (2009) stated that the unit that should be used in CDU modeling is the thermodynamic model BK10 because it is suitable for mixtures of heavier hydrocarbons at pressures under 700 kPa and temperatures from 170°C to 430°C. BK10 is used primarily for crude and vacuum columns operating near atmospheric or subatmospheric pressure (Thermodynamic Data Section, n.d.). The BK10 model can only be used to predict the properties of heavy hydrocarbon systems at low pressures (Doust *et al.*, 2012). According to Aspen Physical Property System (2009), K10 values can be obtained by the Braun convergence pressure method using tabulated parameters for 70 hydrocarbons and light gases. K value is calculated at

system temperature and 10 psia using the Braun convergence pressure method by the model at the given normal boiling point of a component. Then, the K10 value is corrected for pressure using pressure correction charts. K values for any components that are not covered by the charts at 10psia and corrected to system conditions using the pressure correction charts can be found using the modified Antoine equation (Aspen Physical Property System, 2009).

2.5 Types of Mathematical Model

Mathematical modeling problems are often classified into black box or white box models, depending on how much information is available for the system. It is important to choose the right model type when modeling a chemical process so that accurate results can be obtained without wasting computing power and time. Model set selection is determined from the information available. The more the available information, the better the construction of the model and the more the model would resemble its system (Ablameyko, 2003). When choosing the right model type, the flexibility of the model is considered, whether how changes in the design could affect certain aspects of its behavior. A good model designed for long term project needs to be flexible so as to keep up with unexpected design changes. The availability of resources needs to be considered too. In cases where the type of model used is limited by the available computing power, the model needs to be simplified. Finally, the number of approximations that can be safely made must be taken into consideration. Appropriate approximations can greatly increase the efficiency of a model, provided that the approximations do not reduce the model accuracy (Tarr, n.d.). There are three types of modeling, namely black box, grey box and white box.

According to Ablameyko (2003), the black box model is also known as input-output model or empirical model. It is characterized with its input-output behavior without any detailed information about its structure. The elements of a black box model structure have no physical meaning as the model structure does not reflect on the structure of the physical system. Tarr (n.d.) stated that a pure black box model does not describe the internal workings of a device, and that it only solves a numerical problem without reference to underlying physics. Usually, a set of transfer parameters or empirical rules are taken to relate the output of the model to a set of inputs. When the response of a

system is not broken down into its underlying mechanisms, a black box model is used. Black box models are easy to optimize, can run very rapidly and do not require huge computing power as it is a relatively simple model. However, black box model is lacking in flexibility. A lot of work need to be done to determine any new rules or bulk parameters if the model needs to be changed to describe something physically only slightly different. Black box model is also lacking in any form of physical meaning, making it hard to relate the model to the actual device which is being modeled. Black box models come handy when an answer to a specific problem is required while the flexibility to change aspects of a model to see the effect is not required. This model is suitable to be used to provide quick, approximate answers, based on a pre-determined set of input parameters because flexibility is not required as the overall design has already been fixed.

Grey box model is basically the combination of both black box and white box. It provides a physical representation but with some of the physics is approximated (Tarr, n.d.). Most simulation models are grey box models. Grey box model provides more flexibility and enables the use of modeling to optimize a design instead of just providing data based on a fixed design. The internal workings of the design are partly known. Grey box models can be used for design sensitivity analysis, whereby the sensitivity of a design towards a particular aspect is determined.

According to Robinson (2004), a black box model is often the primary test for simulation and its validation should not be relied upon solely. On the other hand, white box model provides a simulation closest to the real behavior of the design being studied. Tarr (n.d.) stated that the white box model is the most detailed type of model and is close to provide a full description of the real device. The method of presentation of a model to its eventual user depends to an extent on how much the knowledge the user knows about the model (An Introduction to Mathematical Modelling, n.d.). Since much information on CDU is obtained through literature, the white box model simulation is used for this research. The physical processes are described at low levels as possible, with no approximations or bulk parameters used so that the simulation would model the actual process accurately. The advantage of using white box models is that they are extremely flexible as everything is modeled at low level. The behavior of the model can be changed in minute detail according to the actual physics. Another advantage is that white box models provide closest match to the real device and models the behavior of a

real device closely to its actual behavior. However, white box models are the most complex types of model to be set up and implemented, which also renders them the slowest running type of model. The complexity of the model requires fast running computers and large memory space. White box model can be used for the same applications as a grey box model but it provides greater realism.

2.6 Modeling Software

There are many commercial process simulators available in the market today. In this research, Aspen Plus will be used in the modeling and simulation of CDU. Aspen Plus is one of the most widely used simulators (Yela, 2009). The steady state model and simulation requirements will be fitted into Aspen Plus. The specification of crude oil and CDU was designed where the model simulation will be done using Aspen Plus (Haydary & Pavlik, 2009).

2.7 Boiling Point Analysis

Petroleum refining industry deals with boiling point ranges. The temperature at which the first vapor formed is called the 'initial boiling point' which corresponds to the bubblepoint of a mixture of specific chemical components (Luyben, 2006). The material will vaporize more if sample heating is continued. The '5% point' is the temperature at which 5% of the original sample has vaporized (Luyben, 2006). The liquid volume percents are more commonly used. The '95% point' is the temperature at which 95 liquid vol% of the original sample has vaporized (Luyben, 2006).

There are three types of boiling point analysis, namely ASTM D86 (Engler), ASTM D158 (Saybolt) and true boiling point (TBP). ASTM D86 is the standard test method for distillation of petroleum products at atmospheric pressure (ASTM International, n. d.). According to Luyben (2006), ASTM D86 and ASTM D158 are similar to the boiling point off vapor as described in the previous paragraph, while in TBP, the vapor from the container passes into a packed distillation column and some specified amount is refluxed. Thus, the TBP analysis exhibits some fractionation while the ASTM analysis is just single-stage separation (Luyben, 2006). ASTM analysis is easier and faster to run while the TBP analysis gives more detailed information about the contents of the crude (Luyben, 2006). Therefore, TBP will be used in this research. Ali & Yusoff (2012)

stated that refining engineers analyze the TBP curves of the 'cuts' present to determine the behavior of the crude distilled and various saleable products. 'Cut points' define the range of boiling points in a given product (Dave, Dabhiya, Ganguly & Saraf, 2003).

Ali & Yusoff (2012) also stated that the TBP curve is one of the most significant characteristic features of the feedstock which decides the amounts of various fractionation products available from the crude as well as the composition and properties of these products. The accuracy and success of property prediction depends mainly on the accuracy of the TBP curve used. Therefore, it is an integral part of the property prediction procedure (Ali & Yusoff, 2012). Commonly, the TBP data of pure crude is available from the crude assay which may not represent the crude being processed at a later time because these deviations may arise due to various reasons like blending of different crudes, contamination of one crude with another in storage tanks or the crude being produced from a different section of the reservoir at different times (Ali & Yusoff, 2012).

2.8 Assumptions and Simplifications

Professional engineering judgment and decisions are important when it comes to making assumptions related to chemical processes. Assumptions are made in order not to complicate matters unnecessary. The followings are assumptions that apply to CDU simulation based on Kumar et al. (2001), Luyben (1990) and Gabriel (2007):

i) Crude oil compositions are expressed in terms of pseudo-components
ii) Dynamic component of condenser and reboiler are negligible
iii) Ideal heat rate balance in absence of interface resistance
iv) Equilibrium temperature is dependent variable
v) Perfect mixing in column and the fluid is incompressible
vi) Heat of mixing is negligible
vii) Fluids are in thermal equilibrium but not phase equilibrium

2.9 Summary of Past Researches

Table 2-1 shows the past researches done related to modelling and simulation of CDU. These past researches done by various researchers are useful in this research as they

provide much information which is used as reference needed in succeeding this research.

Table 2-1 Summary Table for Researches

No.	Research	Validation	Reference
1	Dynamic Simulation of Crude Oil Distillation Plant	Close to real system behavior	Radulescu, G. (2007)
2	CDU Simulation (includes Pre-flash column)	No research data to be compared	Haydary, J., & Pavlik, T. (2009)
3	Dynamic Simulation and Control of ADU	Close to real system behavior	Goncalves, D. D., Martins, F. G., & Feyo de Azevedo, S. (2010)
4	Modeling of Diesel Distillation	Close to lab results	Kumar, S.S (n.d.)
5	Simulation Models in Operations	Close to real system behavior	Schumann, D., Davis, G., & Shah, P. (n.d.)
6	Simulation, control and sensitivity analysis of CDU	Close to real system behavior	Doust, A. M., Shahraki, F., & Sadeghi, J. (2012)
7	CDU suitable for online applications	Valid	Kumar, V., Sharma, A., Chowdhury, I. R., Ganguly, S., & Saraf, D. N. (2001)
8	Simulations of Kaduna Refining & Petrochemical Company CDU Using Hysys	Column need to be optimized	Jibril, M., Folorunsho, A. D., & Manasseh, A. (2012)
9	Simulation of Atmospheric Crude Unit using Aspen Plus	Valid	Stojic, M. M., Nedeljkov, S. L., Krstic, D. M., & Mauhar, S. (2004)

2.10 Summary

This chapter presented the detailed information about crude oil and its classification, the design of CDU, and the importance of models and simulation. The mathematical model

and process simulation involved in this study are discussed. The selection of thermodynamic method is included in this chapter as well. Next, the model types for mathematical model problems and the modeling software, Aspen Plus is reviewed. Then, the boiling point analysis and the assumptions made for this research are also included in this chapter. Lastly, this chapter presented the summary table for the past researches done by other researchers.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Overview

This chapter provides the general procedure and the detailed step by step procedure involved in developing the modeling and simulation of CDU model using Aspen Plus software.

3.2 General Procedure in Modeling

Figure 3-1 shows the general steps involved in developing a simulation of CDU. Generally, to develop a model, the first step is to properly and clearly define the goals and objectives of the research. Then, the steady state CDU model will be simulated after formulating the problem description in mathematical terms and solving the mathematical model using computer software by inserting all the required data into the Aspen Plus software. It is important to build steady state equations for overall composition and enthalpy equations after determining the steady state equation. The steady state equation will be implemented using fundamental equation ODE or AE. Next, the required data for the blending crude will be entered into the simulation using Aspen Plus. The crude feed is important as it could affect the simulation result when

completed. After that, the validity of the simulation must then be checked so that the steady state CDU model obtained is an accurate one. The steady state model is then considered to be complete after the validation is done. After the model is developed, the simulation will be run at different operating conditions and the data will be compared to the plant data available so as to validate the CDU model. The model is considered done if the result is valid.

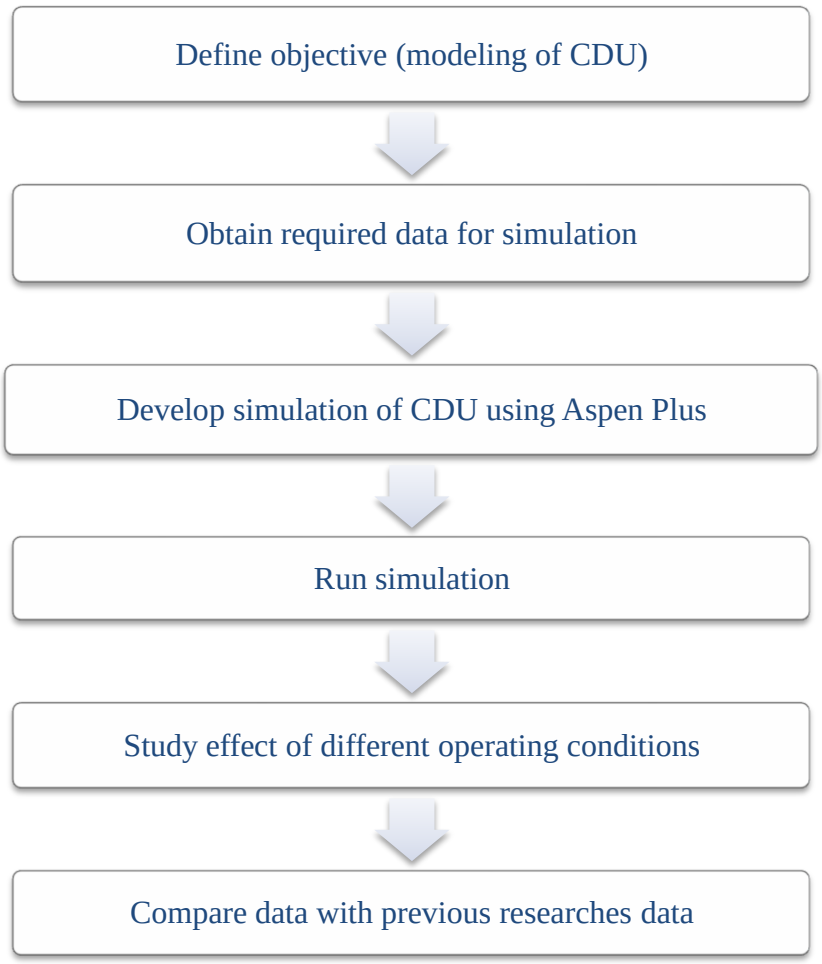

Figure 3-1 General Steps to Develop Simulation of CDU

3.3 Steady State Simulation Using Aspen Plus

The steps in building a steady state model using Aspen Plus is based mainly on Aspen Plus Steady State Simulation: Modeling Petroleum Processes (1997).

3.3.1 Specifying Components, Blend and Pseudocomponents

Firstly, Aspen Plus User Interface is run with Petroleum with English Units template and Assay Data Analysis Run Type selected. This run type will be used to analyze petroleum crudes before running a flowsheet simulation. At the Setup Specifications Global sheet, the title for the simulation is entered as 'Simulation of Crude Distillation Unit (CDU)' and the global settings are double checked to be ENGPETRO units (English Engineering units appropriate for Petroleum applications), StdVol flow basis for all flow inputs and free-water calculations.

After setting up the basics, the components are specified. The components are water, methane, ethane, propane, isobutene, n-butane, 2-methyl-butane and n-pentane. Then, two crude assays, OIL-01 and OIL-02 are defined. Table 3-1 and Table 3-2 show the data of the two crude assays. The data for each assay is entered in a similar way, in the following manner:

i. In the Distillation Curve Type, TBP (liquid volume basis) is selected
ii. For the Bulk Gravity Value, API gravity is selected
iii. API gravity field is entered according to the API gravity of each oil
iv. Light Ends sheet is completed by entering the light ends analysis data
v. Gravity/UOPK sheet is completed entering the API gravity curve data

Then, a blend of the oils is added as OILBLEND. The blend is then defined in terms of assay fraction, which is 0.2 of OIL-01 and 0.8 of OIL-02. The next step involves generating pseudocomponents based on the blend. The pseudocomponent of OILBLEND is named CRUDE and the Specifications sheet is completed.

Table 3-1 OIL-01 (API = 31.4)

Liquid Vol%	Temperature (F)	Component	Liquid Vol Fraction	API Mid. Vol%	API Gravity
6.8	130.0	Methane	0.001	5.0	90.0
10.0	180.0	Ethane	0.0015	10.0	68.0
30.0	418.0	Propane	0.009	15.0	59.7
50.0	650.0	Isobutane	0.004	20.0	52.0
62.0	800.0	n-butane	0.016	30.0	42.0
70.0	903.0	2-methyl-butane	0.012	40.0	35.0

76.0	1000.0	n-pentane	0.017	45.0	32.0
90.0	1255.0			50.0	28.5
				60.0	23.0
				70.0	28.0
				80.0	13.5

(Source: Aspen Plus Steady State Simulation: Modeling Petroleum Processes, 1997)

Table 3-2 OIL-2 (API = 34.8)

Liquid Vol%	Temperature (F)	Component	Liquid Volume Fraction	API Mid. Vol%	API Gravity
6.5	120.0	Water	0.001	2.0	150.0
10.0	200.0	Methane	0.002	5.0	95.0
20.0	300.0	Ethane	0.005	10.0	65.0
30.0	400.0	Propane	0.01	20.0	45.0
40.0	470.0	Isobutane	0.01	30.0	40.0
50.0	550.0	n-butane	0.005	40.0	38.0
60.0	650.0	2-methyl-butane	0.025	50.0	33.0
70.0	750.0	n-pentane		60.0	30.0
80.0	850.0			70.0	25.0
90.0	1100.0			80.0	20.0
95.0	1300.0			90.0	15.0
98.0	1475.0			95.0	10.0
100.0	1670.0			98.0	5.0

(Source: Aspen Plus Steady State Simulation: Modeling Petroleum Processes, 1997)

3.3.2 Preflash Tower

The oil blend enters the preflash furnace where it is partially vaporized before entering the preflash tower as the feed. The PetroFrac block is just the right block to be used to model the furnace and the tower simultaneously. The preflash tower consists of 10 theoretical stages without reboiler, and a partial condenser which operates at 170°F and 39.7 psia with 2 psi pressure drop. The tower which is stripped with open steam in the bottom has a pressure drop of 3 psi. The steam stream has a flow rate of 5 000 lb/hr,

temperature of 400°F and pressure of 60 psia. The preflash furnace operates at 50 psia and 450°F. The distillate rate is estimated at 15 000 bbl/day.

First of all, to model the preflash tower, the Assay Data Analysis run is switched to Flowsheet Run Type at the Setup. A PetroFrac block named PREFL1F is the most suitable block to be used in this case according to the descriptions available on the Help Menu. PREFL1F is selected, renamed as PREFLASH and streams are added to it. Figure 3-2 shows the preflash tower and the streams.

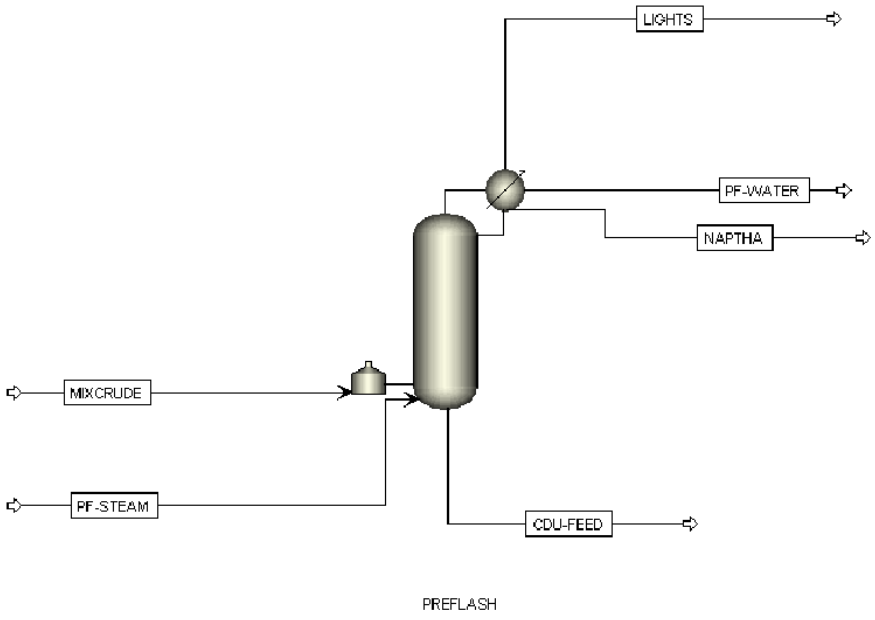

Figure 3-2 Preflash Tower

Secondly, at the Properties Specifications Global sheet, the Property Method BK10 is selected and the Process Type REFINERY is chosen. Other values are not changed as Aspen Plus has already selected the default values.

Thirdly, the streams data are entered. For the MIXCRUDE stream, the temperature is 200F, pressure is 60 psi and flow value is 100 000 bbl/day. For PF-STEAM, the temperature is 400°F, pressure is 60 psi and the water component value (steam flow rate) is 5 000 lb/hr. The Mass-Flow composition is selected to specify the steam flow in lb/hr.

Then, the preflash unit configurations- 10 theoretical stages, Partial-Vapor-Liquid condenser and 15 000 bbl/day distillate rate are entered into the data sheet. As for the

streams, MIXCRUDE has 10 stages with Furnace Convention while PF-Steam has 10 stages with On-stage Convention. In the column, the temperature is 170°F, the top stage pressure is 39.7 psi, second stage is 41.7 psi and bottom stage is 44.7 psi. The furnace is a single stage furnace with a temperature of 450°F and a pressure of 50 psi.

Next, the design specification for the product quality of the naphtha stream is set up using the ASTM 95% temperature (375°F). Then, the number of pseudocomponents generated for different temperature ranges are modified.

3.3.3 Crude Distillation Unit (CDU)

A PetroFrac block CDU10F is chosen to model the CDU tower and its furnace simultaneously. The selected block is placed in the flow sheet and is named as CDU. The furnace, which enters the main fractionator at the 22nd stage, operates at 24.18 psia, with an overflash of 3% in the tower. The main fractionator has 25 stages, a total condenser, a none-bottom feed reboiler and a distillate rate of 13 000 bbl/day. The streams entering and leaving the block are connected to the CDU block as shown in Figure 3-3. The steam streams entering the tower and strippers have temperature of 400°F and pressure of 60 psi, with mass flow rate of 12 000 lb/hr for DU-STM, mass flow rate of 3 300 lb/hr for DU-STM1, mass flow rate of 1 000 lb/hr for DU-STM2 and mass flow rate of 800 lb/hr for DU-STM3.

After specifying all the tower and streams details, the strippers and pumparounds data are entered according to Tables 3-3 and Table 3-4 which show the specifications for the pumparounds and strippers respectively.

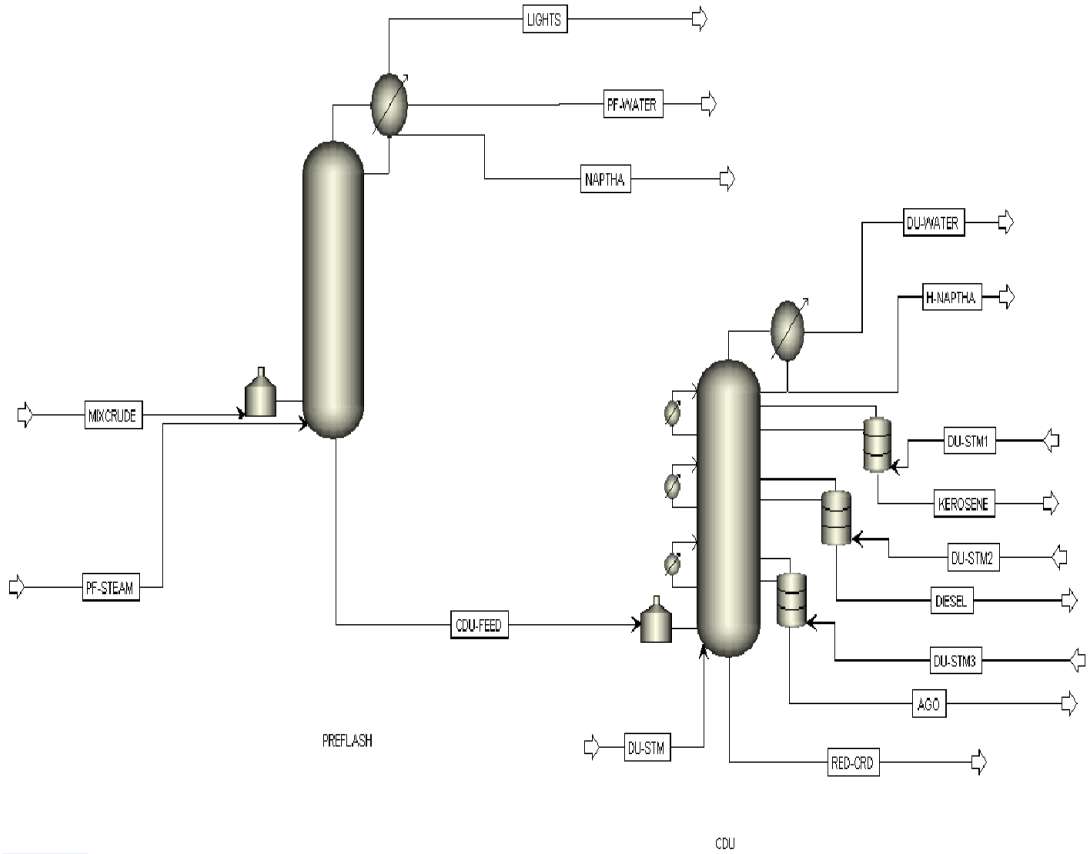

Figure 3-3 Preflash Column and CDU

Table 3-3 Pumparound Specifications

Pumparound	Location	Specifications
1	Stage 8 to 6	Flow: 49 000 bbl/day; Duty: -40 MMBTU/hr
2	Stage 14 to 13	Flow: 11 000 bbl/day; Duty: -15 MMBTU/hr

Table 3-4 Stripper Specifications

Stripper	Location	Specifications
Kerosene	Liquid draw from stage 6, vapor return to 5	Rate: 11 700 bbl/day; 4 equilibrium stages
Diesel	Liquid draw from stage 13, vapor return to 12	Rate: 16 500 bbl/day; 3 equilibrium stages
AGO	Liquid draw to stage 18, vapor return to 17	Rate: 8 500 bbl/day; 2 equilibrium stages

3.3.4 Vacuum Distillation Unit (VDU)

The function of a VDU is to separate the reduced crude from the CDU into off-gas, light vacuum gas oil, heavy vacuum gas oil and residual vacuum oil. This VDU consists of a furnace and a tower of six stages.

Firstly, PetroFrac block VACUUM1F is placed in the flowsheet and is named as VDU. The streams entering and leaving the block are placed as shown in Figure 3-4. Figure 3-4 also shows the complete set of blocks and streams involved in this simulation. The specifications of the tower, data of each of the streams, and specifications of the two pumparounds are then entered into Aspen Plus respectively. The steady state simulation can now be run.

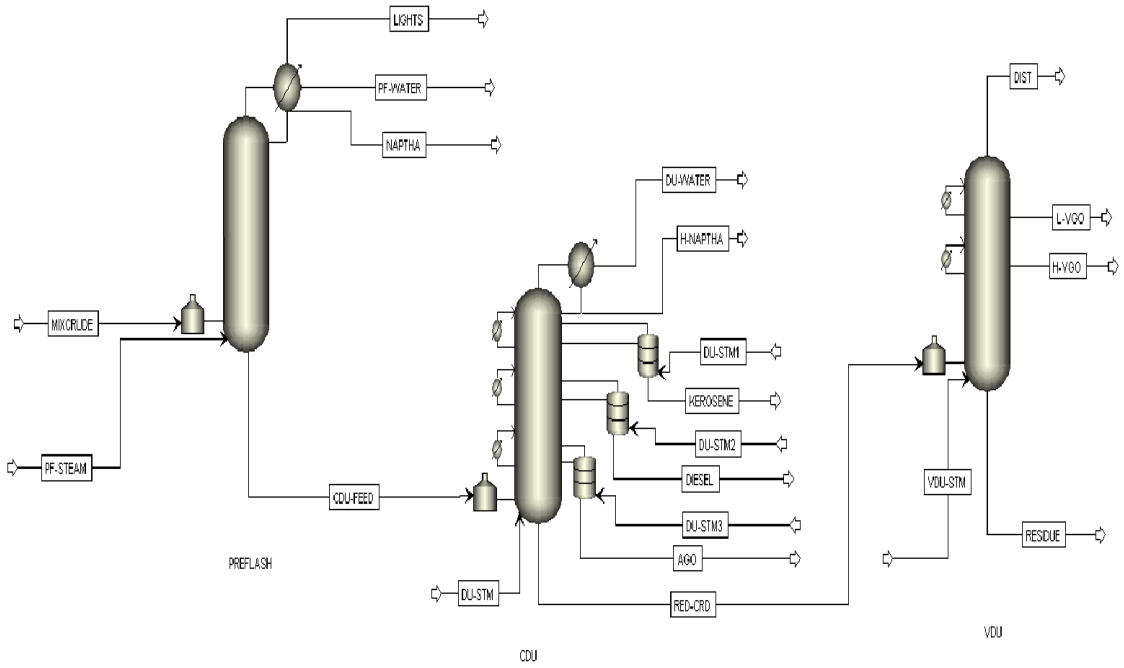

Figure 3-4 Complete Set of Blocks and Streams

3.3.5 Sulfur Content

As mentioned before in Chapter 1, crude oil consists of sulphur. So, it is important to add the data of sulfur content into the simulation as well. The sulfur property values are added for OIL-01 and OIL-02 respectively as the final step in developing this simulation model. The steady state model is now complete.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Overview

This chapter presents the result obtained from the completed CDU simulation. The result is illustrated in the form of graphs and tables, and are discussed and compared with previous researches done by past researchers.

4.2 Mathematical Model

Theoretical stage method is usually used for mathematical description of a distillation process in refining columns (Haydary & Pavlik, 2009). The mass balance of individual components, pseudocomponents, enthalpy balance, and vapor-liquid equilibrium equations all together create the mathematical model of a theoretical stage (Haydary & Pavlik, 2009). The mathematical model of a column consists of models of individual theoretical stages.

4.2.1 Mass Balance

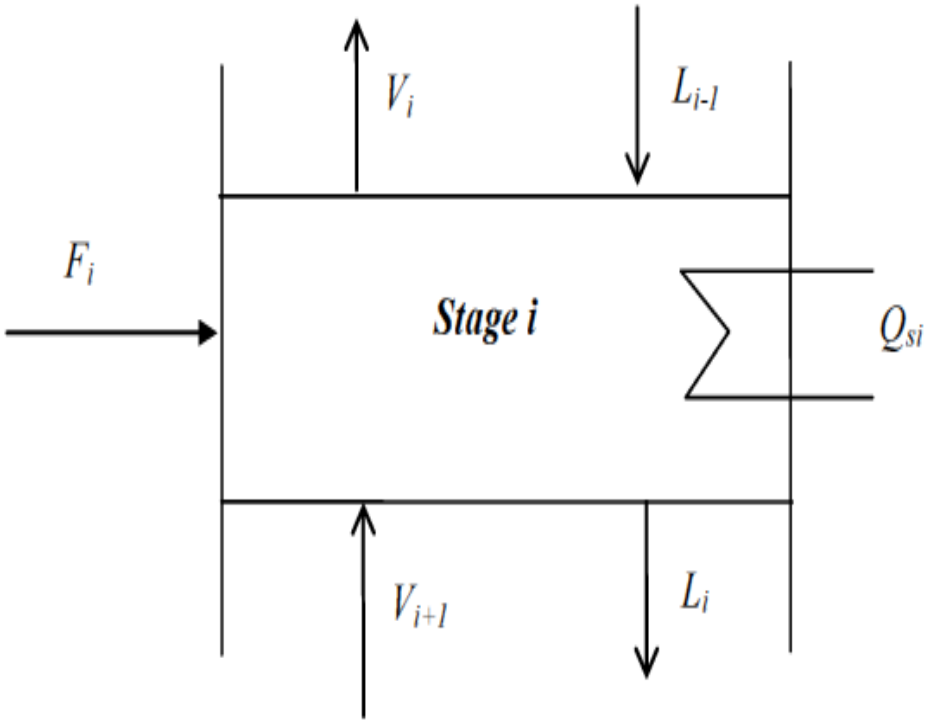

Figure 4-1 Scheme of a Column Stage

The steady state mass balance of stage i and component j is can be described as in Equation 4-1:

$$L_{i-1}x_{i-1,j} + V_{i+1}y_{i+1,j} + F_if_{i,j} - L_{i,j}x_{i,j} - V_iy_{i,j} = 0 \qquad \text{(Equation 4-1)}$$

where V_i is the molar flow of vapor from stage i, V_{i+1} is the molar flow of vapor entering stage i, L_i is the molar flow of liquid from stage i, L_{i-1} is the molar flow of liquid entering stage i, x, y, and f represent the molar frictions in liquid, vapor and feed respectively. Figure 4-1 represents the general scheme of a stage.

In dynamic state, the right side of Equation 4-1 represents accumulation of mass on the stage, as shown in Equation 4-2:

$$L_{i-1}x_{i-1,j} + V_{i+1}y_{i+1,j} + F_if_{i,j} - L_{i,j}x_{i,j} - V_iy_{i,j} = \frac{d(W_ix_{i,j})}{d\Theta} \qquad \text{(Equation 4-2)}$$

where W_i represents the liquid holdup on the stage. At pressures lower than 10 atm, the holdup of the vapor phase is negligible as it is less than 20% of the liquid holdup (Haydary & Pavlik, 2009).

$$W_i = \rho_{Li} A_{Ti} h_{Ti} + \rho_{Li} A_{Di} h_{Di} \quad \text{(Equation 4-3)}$$

Equation 4-3 is used for calculation of liquid holdup on the stage, where ρ_{Li} is the density at stage i, A_{Ti} is the stage active surface area, h_{Ti} is the liquid height on stage i, A_{Di} is the downcorner surface area and h_{Di} is the liquid height in the downcorner.

Next, Equation 4-4 is the Francis equation which can be used to calculate the molar flow of liquid from stage i, where c is a constant value of 042, l_{Wi} is the weir length, and h_{Wi} is the weir height.

$$L_i = c\sqrt{2g} l_{Wi} \rho_{Li} (h_{Ti} - h_{Wi})^{1.5} \quad \text{(Equation 4-4)}$$

4.2.2 Enthalpy Balance

Enthalpy balance for steady state stage i is shown in Equation 4-5. h_i, h_{i+1}, h_{i-1} and h_F are the molar enthalpies of corresponding streams, Q_M is the heat of mixing, Q_S is the external heat source and Q_{loss} is the heat lost.

$$L_{i-1}h_{i-1} + V_{i+1}h_{i+1} + F_i h_{Fi} - L_i h_i - V_i h_i + Q_M - Q_S - Q_{loss} = 0 \quad \text{(Equation 4-5)}$$

As for dynamic state, the right side of the equation represents the heat accumulation on stage i, as shown in Equation 4-6.

$$L_{i-1}h_{i-1} + V_{i+1}h_{i+1} + F_i h_{Fi} - L_i h_i - V_i h_i + Q_M - Q_S - Q_{loss} = \frac{d(W_i h_i)}{d\theta} \quad \text{(Equation 4-6)}$$

4.2.3 Vapor-Liquid Equilibrium

Assuming that the vapor and liquid phases are in equilibrium, the general equilibrium equation is as in Equation 4-7, where K_j is the equilibrium constant for component j.

$$y_j = K_j x_j \quad \text{(Equation 4-7)}$$

4.3 Convergence of Simulation Results

By entering all the initial conditions into the simulation software, the results will converge towards a steady state condition. Figure 4-2 shows that the simulation was successfully run smoothly without any errors.

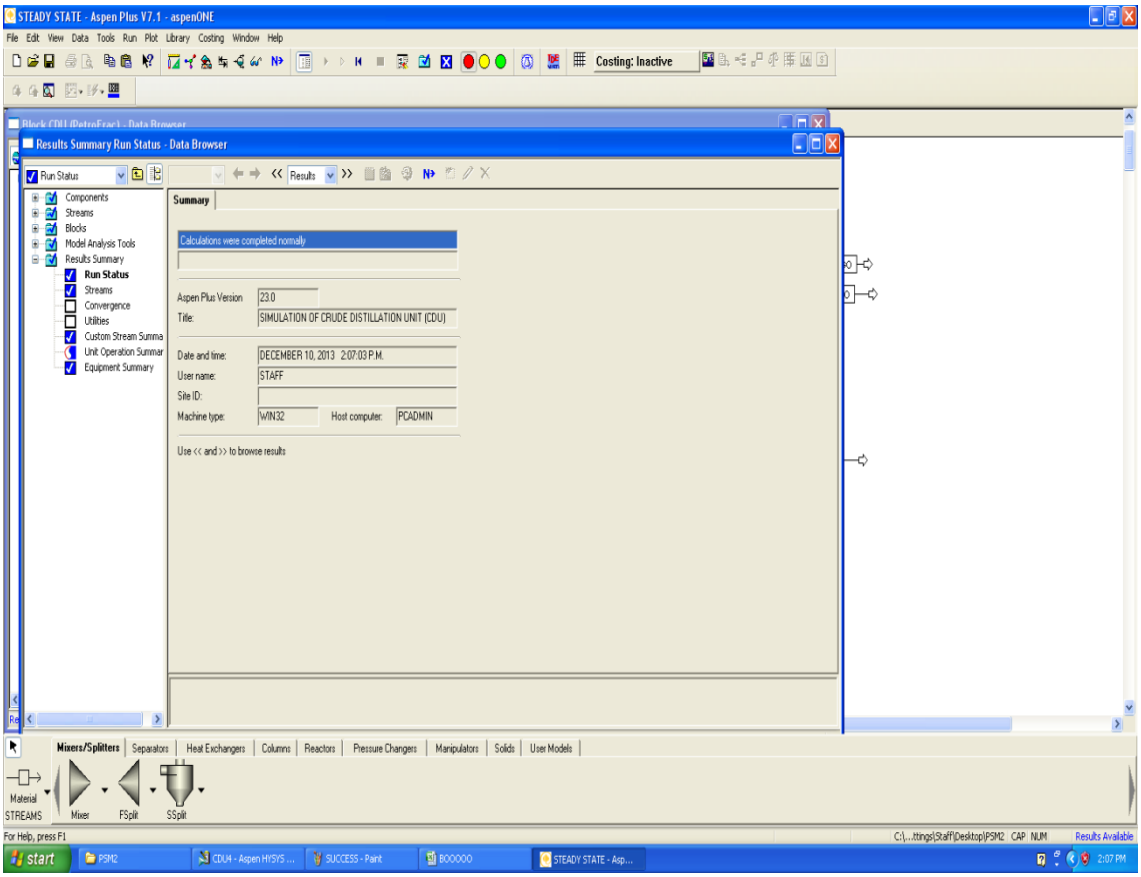

Figure 4-2 Steady State CDU Simulation Successfully Run Without Error

Using the successfully developed CDU simulation model, many data of the system in study can be obtained effortlessly. For example, the pressure, temperature, enthalpy, heat duty, components liquid and vapor compositions, liquid and vapor flow rates in each stage of each unit can be obtained from the results browser of the simulation.

Figures 4-3 and 4-4 show the pressure in each stage of the units of Preflash and CDU respectively. The stage numbers are numbered from the top stage (Stage 1) to the bottom stage (last stage) in the columns. The figures show that when we descend (ascending stage number) along the Preflash and CDU columns, the pressure in the columns increased. For both Preflash and CDU, the highest pressure stage is in the bottom most stage, while the lowest pressure stage is in the first stage or the top stage.

In the Preflash, the highest pressure is at 44.7 psia and the lowest pressure is at 39.7 psia. Meanwhile, in the CDU, the highest pressure is at 24.7 psia and the lowest pressure is at 15.7 psia. According to Clarkson University (2012), the pressure in a distillation column must decrease when going up the column, which fits perfectly with the data obtained from this CDU simulation.

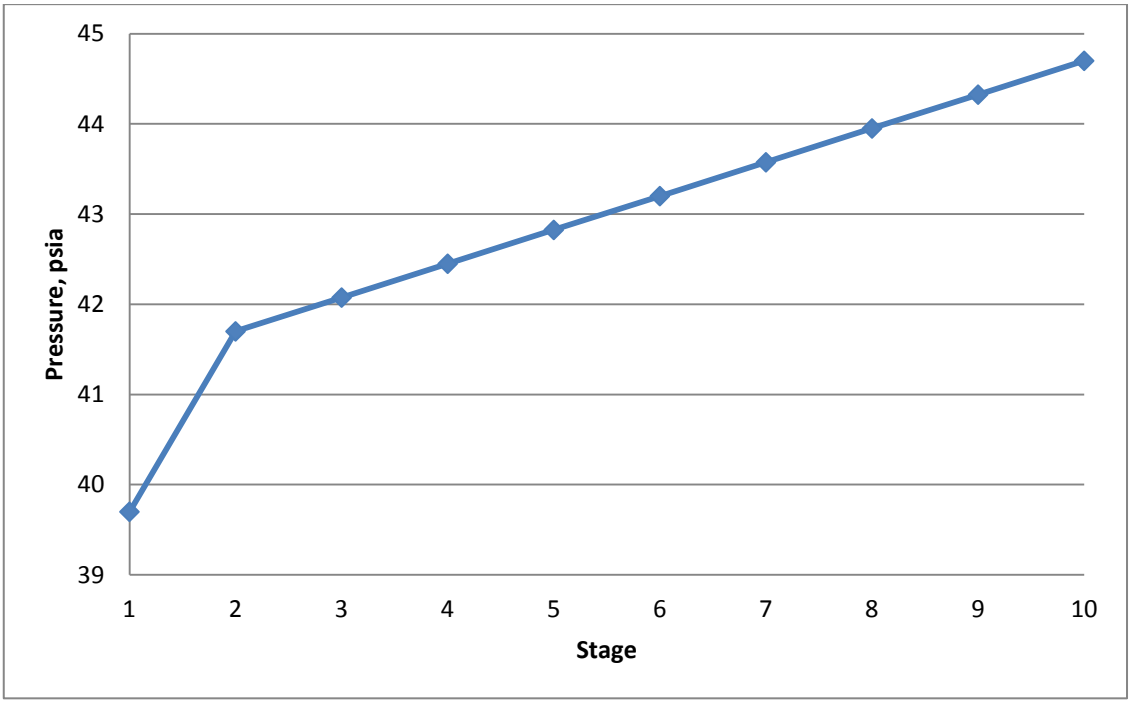

Figure 4-3 Stage Pressure in Preflash

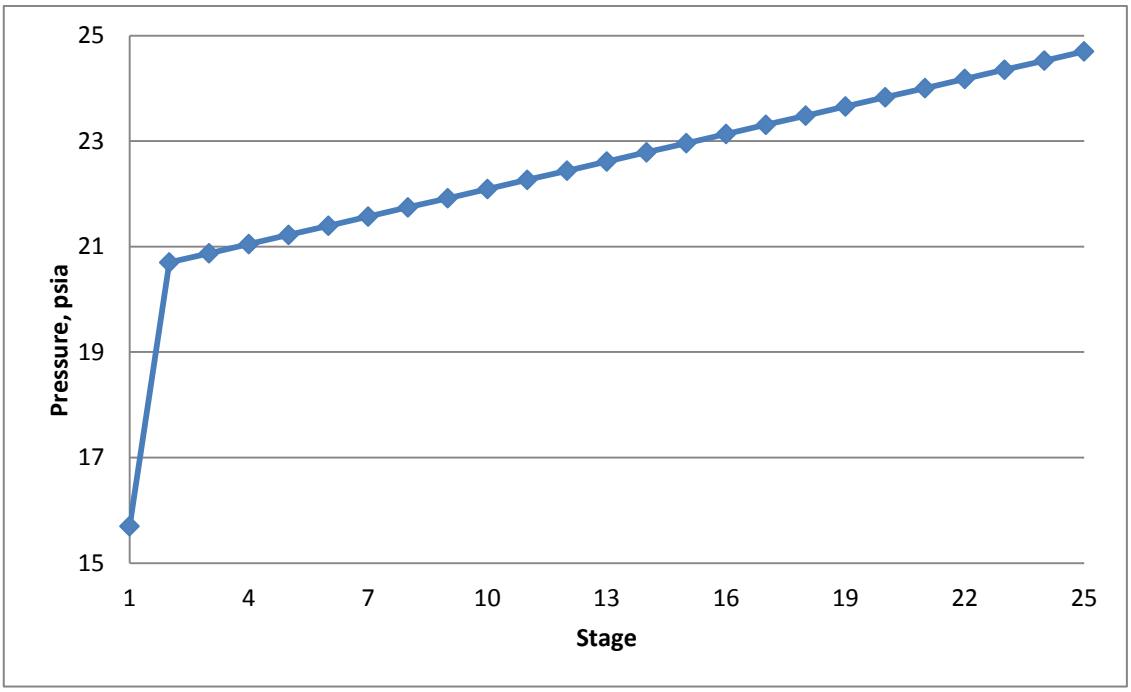

Figure 4-4 Stage Pressure in CDU

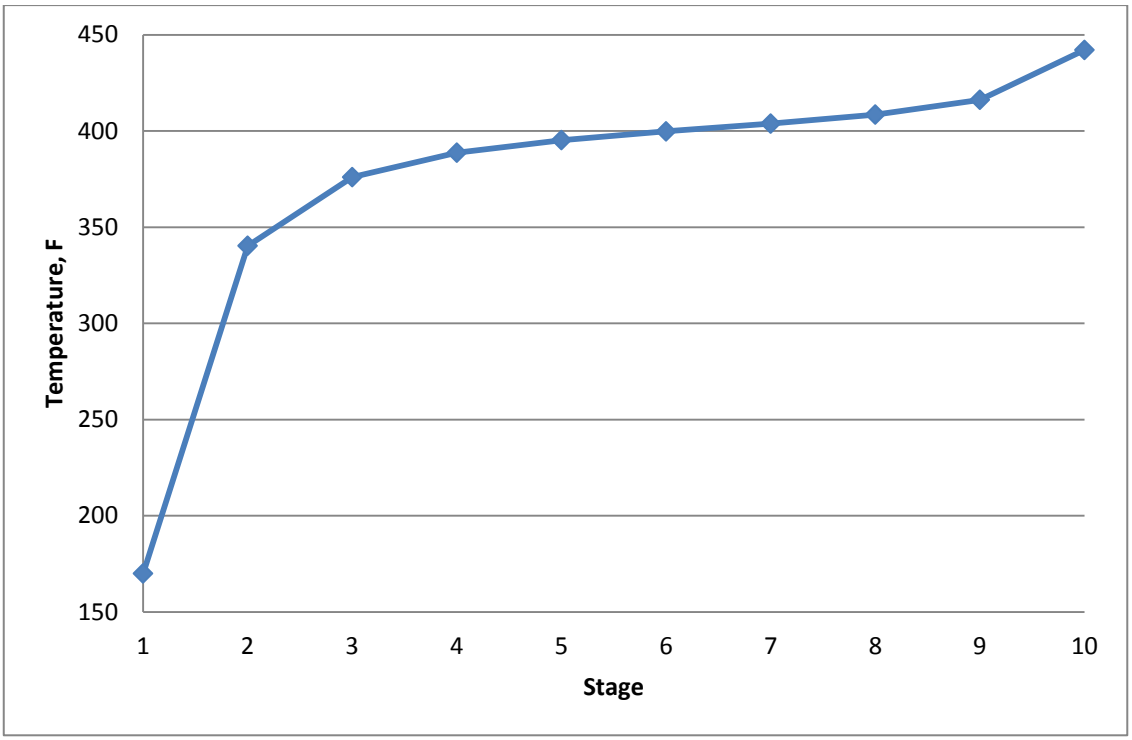

Figure 4-5 Stage Temperature in Preflash

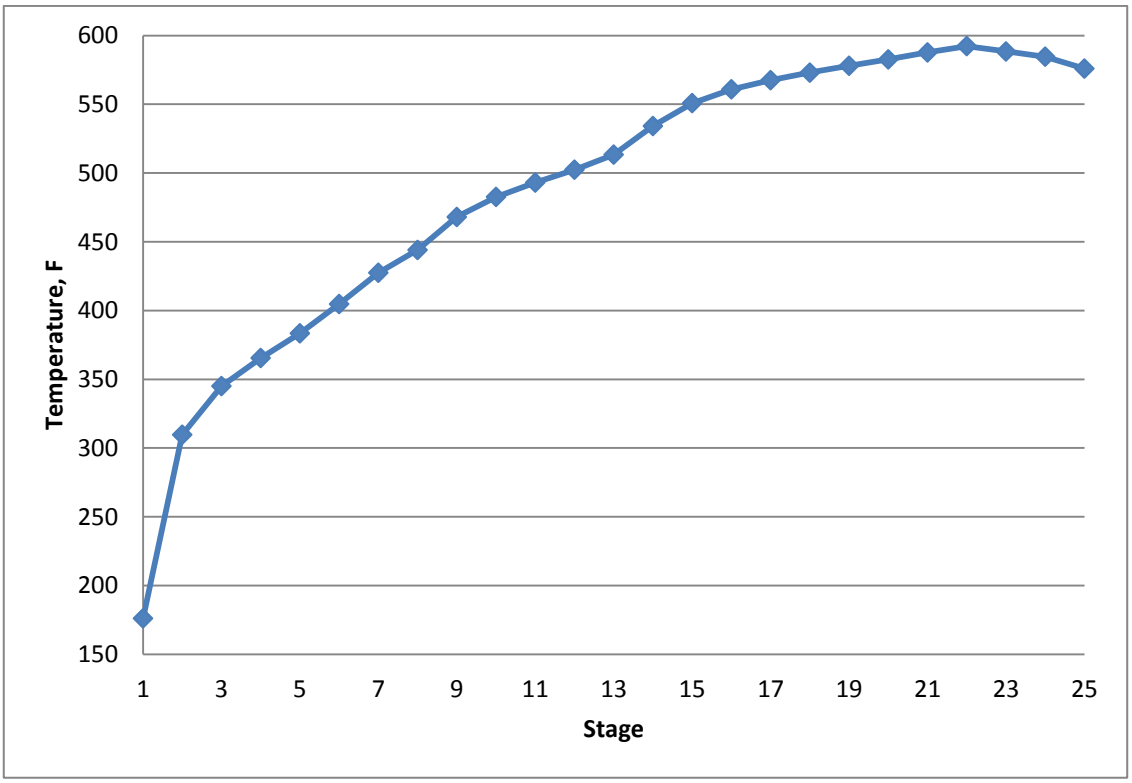

Figure 4-6 Stage Temperature in CDU

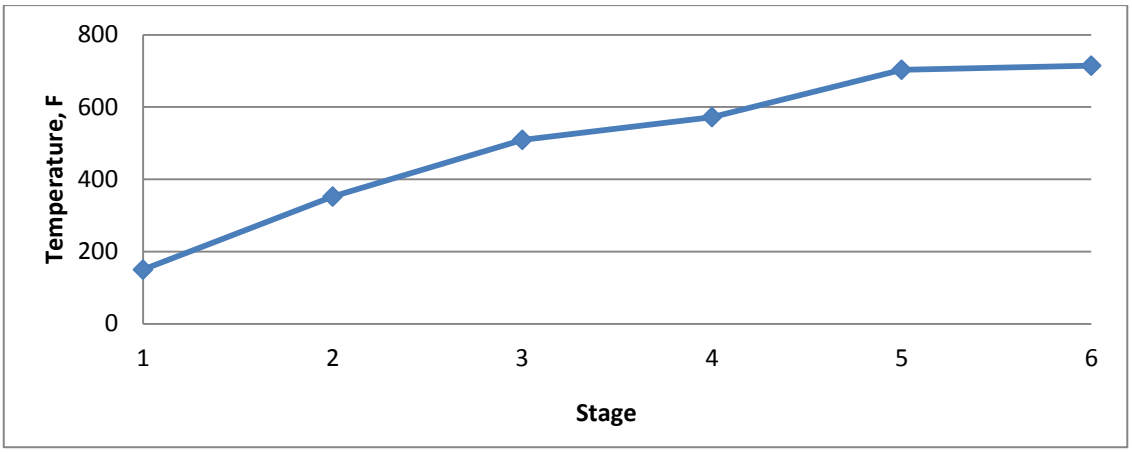

Figure 4-7 Stage Temperature in VDU

Figures 4-5, 4-6 and 4-7 show the temperature in each stage of the units of Preflash, CDU and VDU respectively, From Figures 4-5 to 4-7, it can be seen that the temperature increased as we go down (stages numbered from the top stage to the bottom stage) along the stages in each of the units. The lowest temperature in Preflash is 170.0°F in Stage 1, while the highest temperature is 442.1°F in Stage 10 (last stage). For CDU, the temperature increased from 176.2°F in Stage 1 to the highest 592.32°F in stage 22, and slowly decreased to 576.0°F in the last stage (Stage 25). For VDU, the lowest temperature is at 150°F in the first stage and the highest temperature is at 714.4°F in the last stage (Stage 6).

In fractional distillation, as the vapor ascends the unit column, it encounters a cooler area and condenses. The hot ascending vapors revaporize the liquids and the vapour travels further up the column, where it encounters a cooler area and recondenses back into liquid (University of Massachusetts Amherst, 2012). So the temperature gradually decreases as we go up the column, condensing the heaviest hydrocarbons at the bottom and the lightest hydrocarbons at the top (Energy Institute, n. d.).

Figures 4-8 and 4-9 show the components vapor and liquid compositions in each stage of the Preflash unit respectively. For the vapor composition, all the components have highest composition in Stage 1 and lowest in Stage 10, except for water. Water has highest composition in the last stage. Water also has the highest composition in Preflash compared to other components. For liquid composition, the highest composition component is n-pentane. Like the vapour compositions, the components have highest composition in Stage 1 and lowest in the last stage, except for water. Water has highest

composition in Stage 1 and lowest in Stage 9. At Stage 10, composition of water increased.

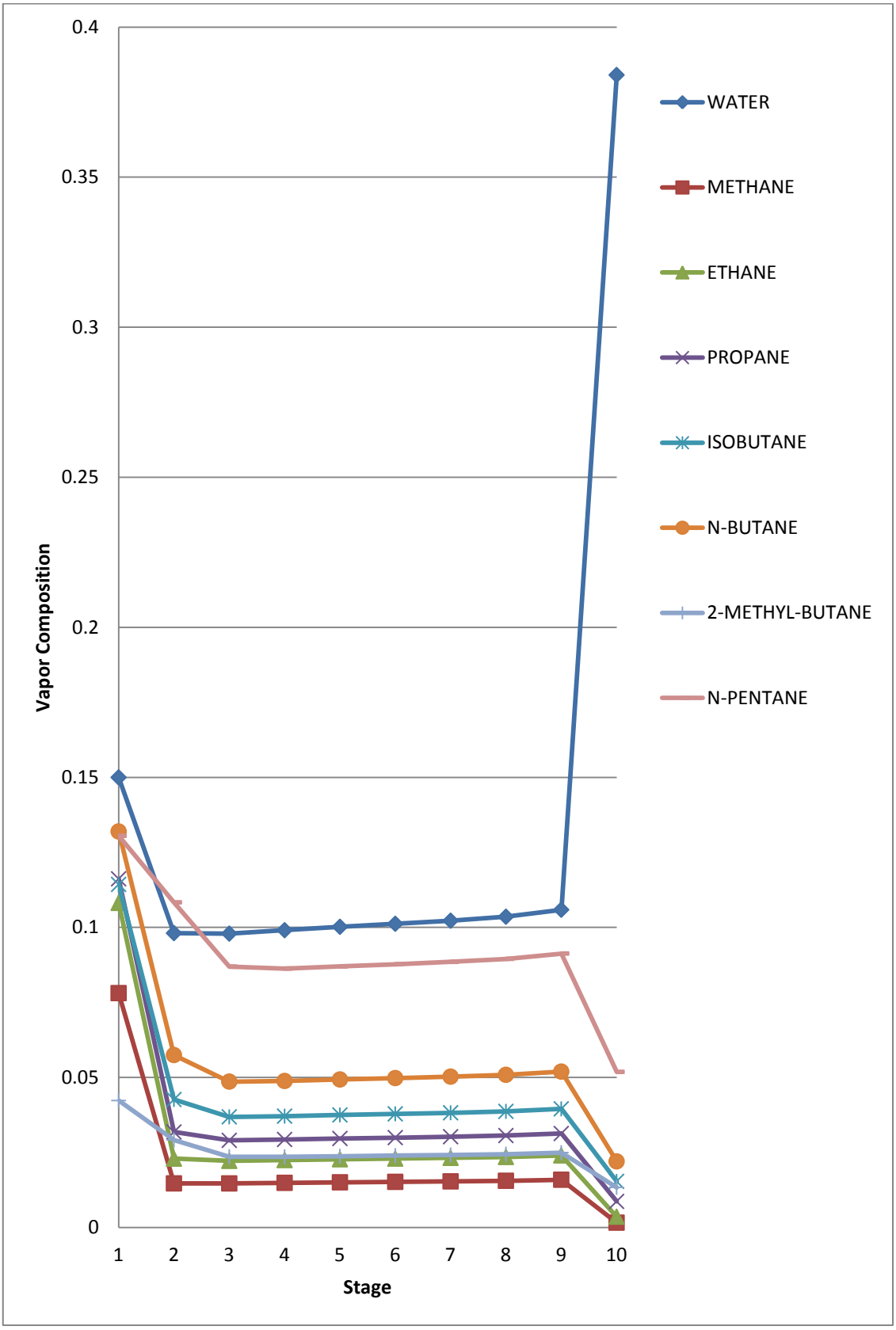

Figure 4-8 Stage Components Vapor Compositions in Preflash

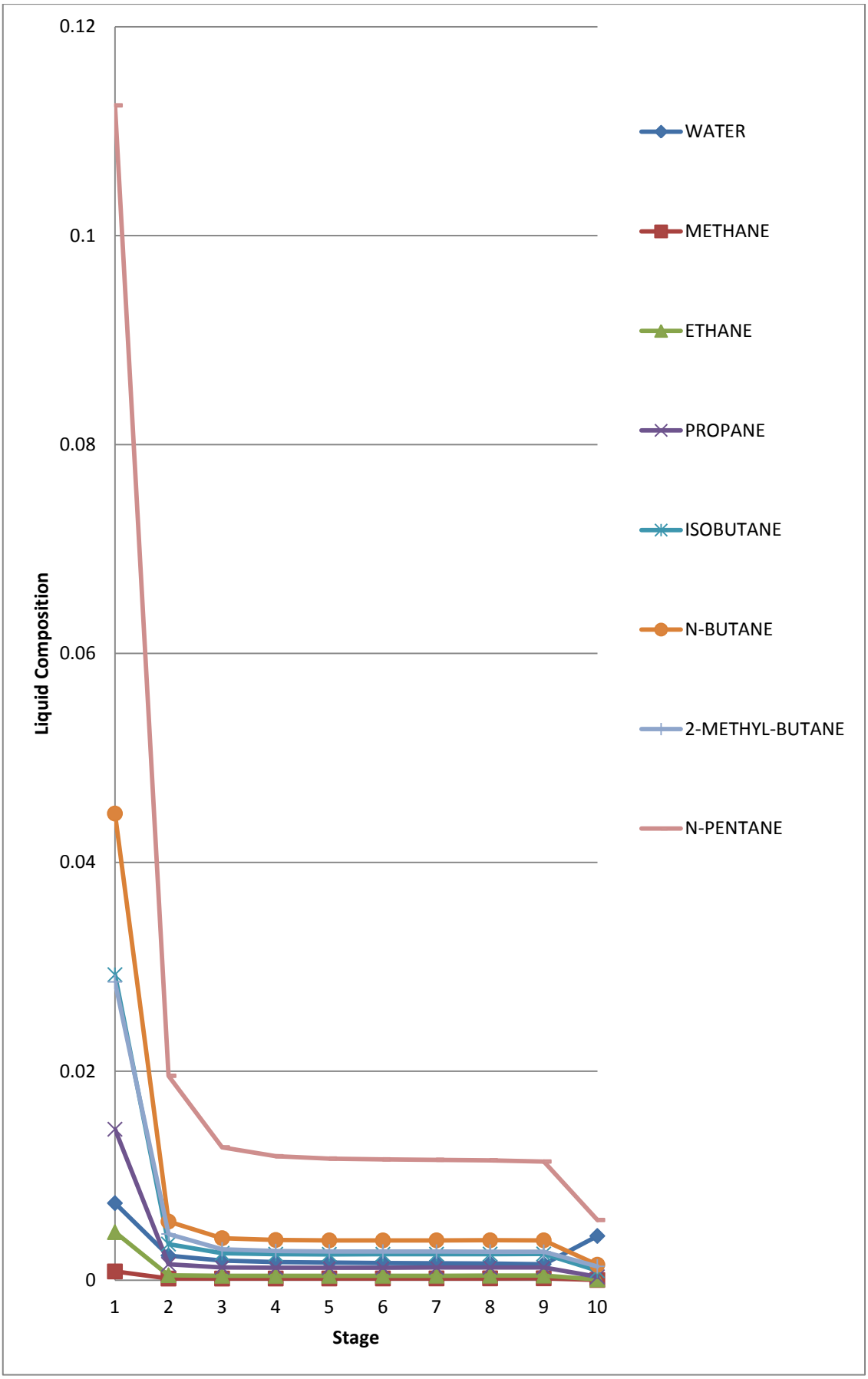

Figure 4-9 Stage Components Liquid Compositions in Preflash

4.4 Validation of Simulation Data

Table 4-1 Comparison of Simulation Data with Literature Data from Chatterjee & Saraf (2004)

Data	Simulation Data	Literature Data	Error (%)
Feed Flow Rate (m^3/h)	1080.2	1080.2	-
Product Flow Rate (m^3/h):			
Heavy Naphtha	92.51	199.20	53.55
Kerosene	170.63	128.00	24.98
AGO	18.82	32.40	41.91

Table 4-1 shows the comparison between simulation data with the data obtained from literature Chatterjee & Saraf (2004). A feed flow rate 1080.2 m^3/h was used in both and the products flow rates were compared. The difference in value for heavy naphtha shows 53.55%, for kerosene is 24.98% and for AGO is 41.91%. This literature used only one unit for the simulation while three units were used in this research, therefore, the percentage of error is quite high. Besides, the crude oils used in both research were different and each crude oil has its own characteristics and components of different compositions as well as sulphur content. The simulation is proved to be valid despite the errors as the operating conditions were not the same. Ali & Yusoff (2012) stated that even a small change in the operating condition could cause a huge change for the relevant data of products. Therefore, the simulation is validated.

4.5 Effect of Change in Feed Flow Rate on Products Flow Rates

In steady state condition, when the feed, MIXCRUDE, flow rate is increased while keeping the heat supplied and heat loss constant, the heat of mixing is assumed negligible. Then, the product flow rate is proportional to the feed flow rate, as shown in Equation 4-8.

$$L_{i-1}h_{i-1} + V_{i+1hi}+1 + F_ih_{Fi} + Q_M = L_ih_i + V_ih_i + Q_S + Q_{loss} \quad \text{(Equation 4-8)}$$

To study this effect of feed flow rate change on products flow rates, the initial feed flow rate for the simulation, 100 000 bbl/day is changed to 150 000 bbl/day and 200 000 bbl/day. Then, the flow rates of products from the Preflash column, CDU and VDU are generated and compared. The results obtained is shown in Table 4-2, while Figure 4-10

shows the graph of products flow rates at three different feed flow rates, where H-NAPHTHA stands for heavy naphtha, AGO for atmospheric gas oil, RED-CRD for reduced crude, L-VGO for light vacuum gas oil, and H-VGO for heavy vacuum gas oil.

From Figure 4-10, it is observed that AGO and H-VGO do not show significant increment with the increase in feed flow rate. The product which shows the most significant change is RED-CRD and it is also the product with the highest flow rate despite the change in feed flow rate. It can be summarized from Figure 4-10, that the products flow rates increased as the feed flow rate is increased. The higher the feed flow rate, the higher the products flow rates. This proves that the simulation is valid as it follows the literature which states that the products flow rates of a steady state model column with constant tray efficiencies will scale directly with the column feed flow rate (Riggs, 1992).

Table 4-2 Products Flow Rates at Different Feed Flow Rates (all values in bbl/day)

Feed ($x10^{-3}$)	H-Naphtha	Kerosene	Diesel	AGO	Red-Crd	Naphtha	L-VGO	H-VGO	Residue
100	7344.66	16025.20	9346.79	1528.30	45589.40	16572.20	15454.30	17000.00	13090.60
150	12070.70	23744.60	13120.30	2445.51	69210.00	23931.60	27893.40	17000.00	24221.80
200	16819.38	31424.70	16824.20	3387.55	93031.00	31148.80	38655.60	17000.00	37227.20

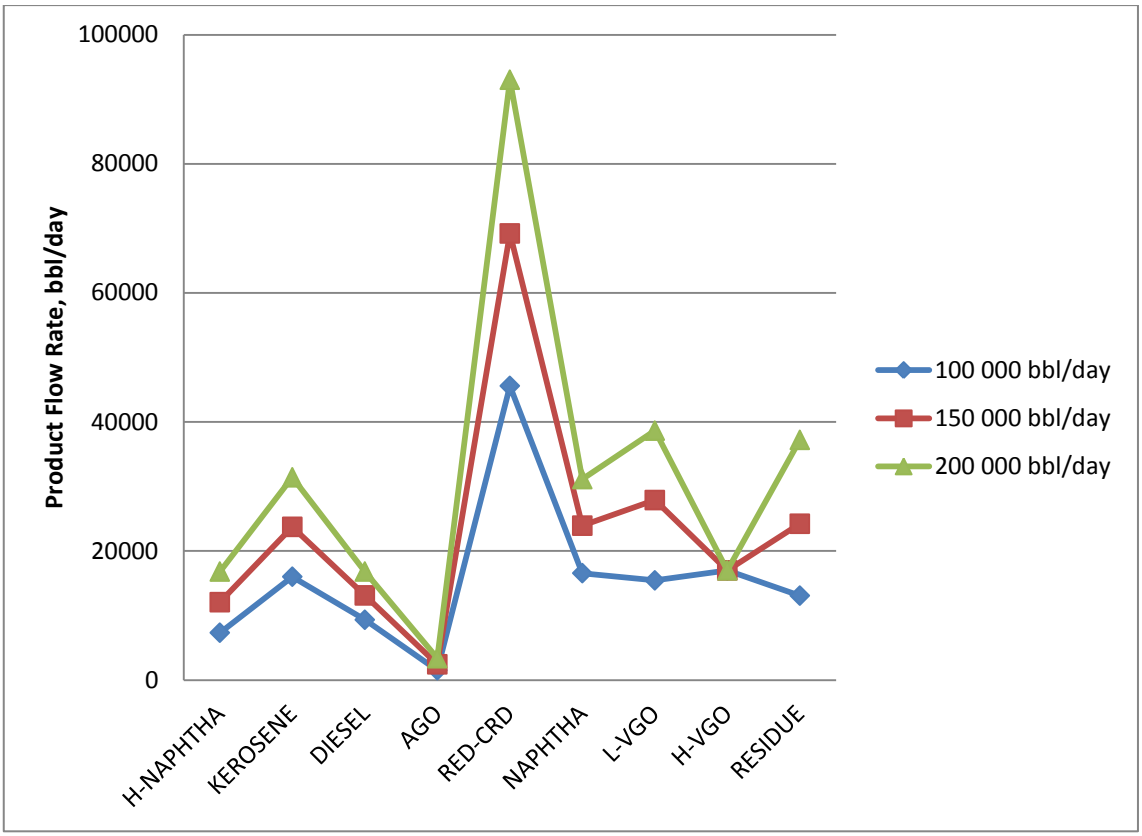

Figure 4-10 Effect of Feed Flow Rate to Products Flow Rates

However, the change in each products flow rates is not the same even though the increment of feed flow rate is of the same value, which is 50 000 bbl/day. The percentage of different changes in products flow rates can be seen in Table 4-3. This unpredictable change highlights the importance of having a CDU simulation as a CDU model can make the calculations much easier and faster. Instead of generating the values of change manually using the sets of mathematical equations mentioned earlier, generating the values using a CDU model only takes a minute or two and is just a few clicks away.

Table 4-3 Percentage of Products Flow Rates Change

Feed ($x10^{-3}$ bbl/day)	H-Naphtha (%)	Kerosene (%)	Diesel (%)	AGO (%)	Red-Crd (%)	Naphtha (%)	L-VGO (%)	H-VGO (%)	Residue (%)
From 100 to 150	64.35	35.20	40.37	60.01	51.81	44.41	80.49	0.000003	85.03
From 150 to 200	39.34	32.34	28.23	38.52	34.41	30.16	38.58	0.0001	53.69

4.6 Standard Distillation Test Method

ASTM D86 data of products were available for each unit (Preflash, CDU and VDU). Figure 4-11 shows the graph of volume of CDU products distilled at different temperatures using the ASTM D86 method. The total percent volume of products distilled was plotted against temperature in the CDU. From the figure, it can be seen that the volume percent of reduced crude distilled is at the highest temperature compared to other products. This is because the reduced crude is the heaviest product coming out of the CDU or in other words, it has highest boiling point. The law of distillation is that the component of lowest melting point is distilled first, followed by the second lowest boiling point component and so on. This means that reduced crude is the last to be distilled. From Figure 4-11, the first product to be distilled at lowest temperature is heavy naphtha, followed by kerosene, diesel, AGO and finally, reduced crude.

The same principle applies to the Preflash and VDU. The lower the temperature, the faster the product is distilled and the lower boiling point it has. Figure 4-12 shows the graph of temperature against volume of products distilled for Preflash, while Figure 4-13 is for VDU. From each of the figures (Figure 4-11 to Figure 4-13), the percentage of volume of products distilled at a certain temperature or the temperature at which a certain volume of products distilled can easily be identified. The sequence of products being distilled can be obtained from Figure 4-11 to Figure 4-13 too.

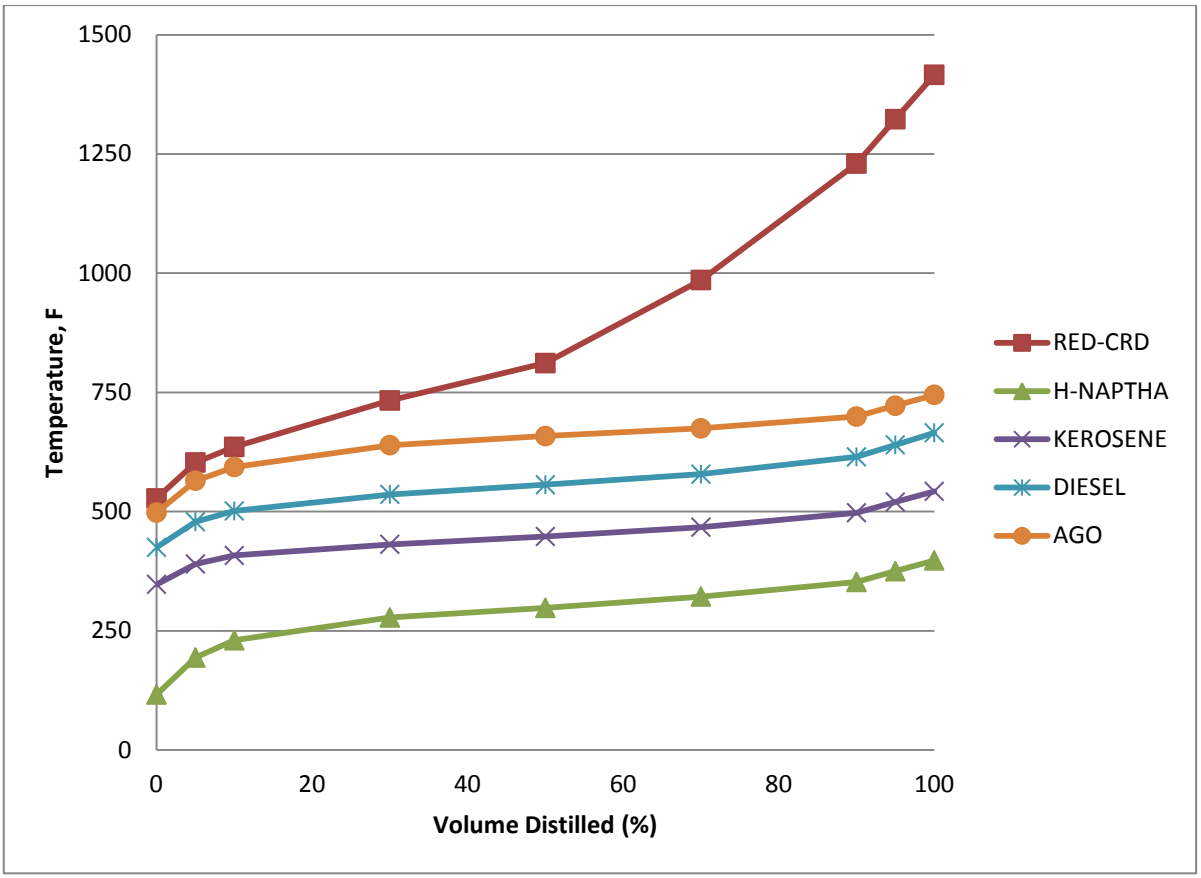

Figure 4-11 Volume of CDU Products Distilled using ASTM D86

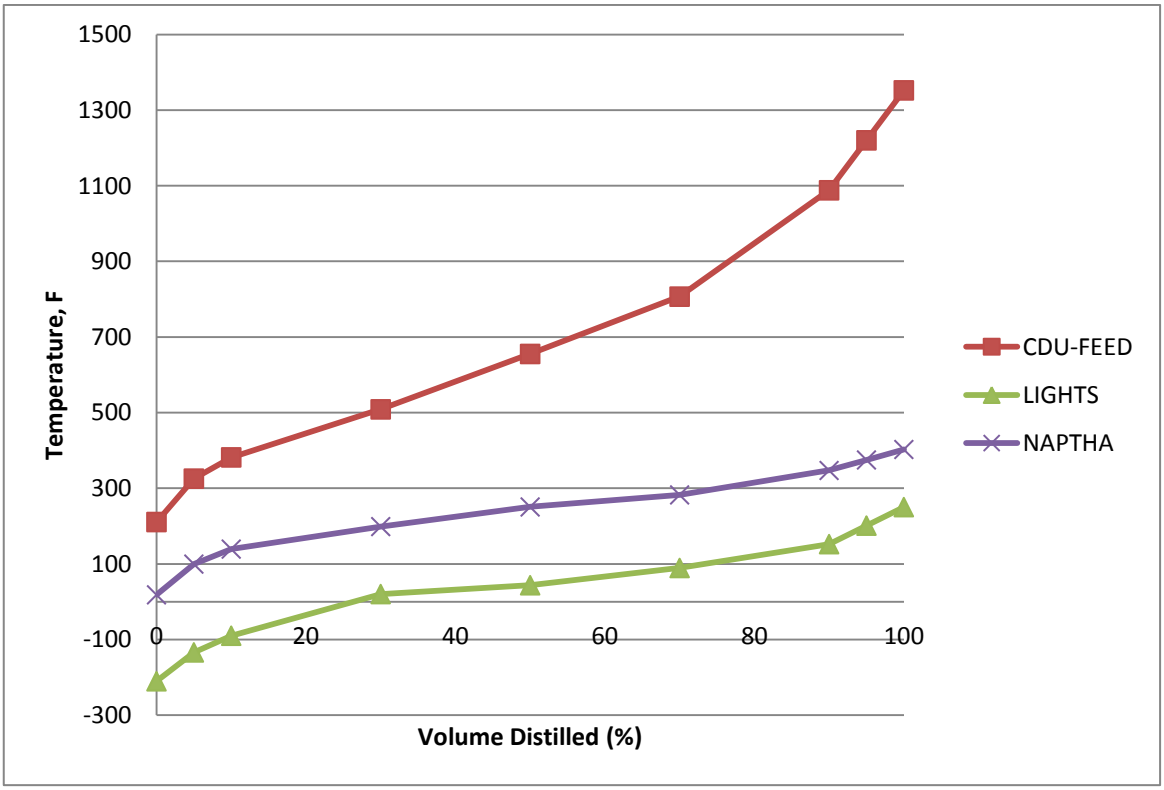

Figure 4-12 Volume of Preflash Products Distilled using ASTM D86

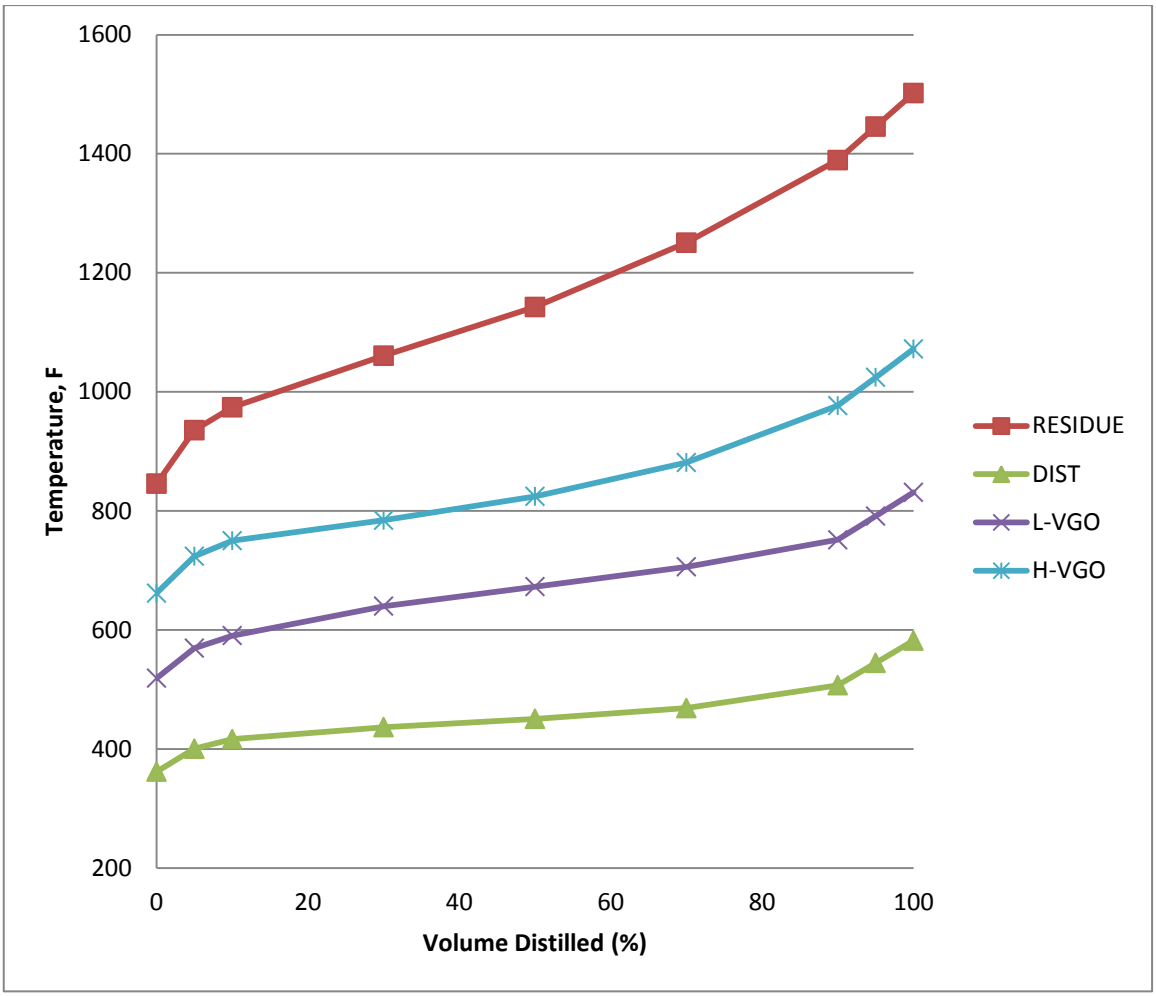

Figure 4-13 Volume of VDU Products Distilled using ASTM D86

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The modeling and simulation of CDU in this research was successfully converged as results that follow literature theory are obtained. The pressure and temperature in each of the three units increases as we go down the columns. These results follow the literature which states that the temperature and pressure in a distillation column should decrease when going up the column. Next, when the feed flow rate was increased, the products flow rates increased as well. Besides that, using the ASTM D86, the volume of products distilled at different temperatures was obtained. In Figures 2 to 4, it was proven that the model follows the distillation law which states that component with lowest boiling point will be distilled first. Various information about the system under study can be obtained through this simulation model of CDU. The model was also compared with previous research on its validity and has been proven to be valid.

The objectives were achieved as a model of CDU was developed and the effect of different operating conditions of petroleum refining toward the yield and composition of petroleum products was studied.

Future studies are recommended to analyze the effect of more different operating conditions towards the yield and composition of products such as changing the pressure or property method, and adding or removing equipments for a better understanding of the system. Comparison of using different blends of oils should also be studied for observation of different components compositions.

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APPENDICES

Tables A-1, A-2 and A-3 are summary tables showing results obtained from the simulation for Preflash, CDU and VDU respectively.

Table A-1 Summary Table for Preflash

Stage	Temperature (F)	Pressure (psia)	Heat duty (MMBtu/hr)	Liquid flow (lbmol/hr)	Vapor flow (lbmol/hr)
1	170.0012	39.7	-63.318	2552.478	609.2729
2	340.3263	41.7	0	769.9918	3383.428
3	375.9918	42.075	0	727.0622	3346.796
4	388.7055	42.45	0	688.0569	3303.867
5	395.2556	42.825	0	654.6843	3264.862
6	399.7783	43.2	0	621.2977	3231.489
7	403.8285	43.575	0	579.7865	3198.102
8	408.5287	43.95	0	509.3706	3156.591
9	416.2093	44.325	0	247.1753	3086.175
10	442.1041	44.7	0	3869.161	684.4077

Table A-2 Summary Table for CDU

Stage	Temperature (F)	Pressure (psia)	Heat duty (MMBtu/hr)	Liquid flow (lbmol/hr)	Vapor flow (lbmol/hr)
1	176.171	15.7	-66.0041	2046.146	0
2	309.7081	20.7	0	1578.556	2997.25
3	345.0928	20.87391	0	1555.639	3231.387
4	365.5064	21.04783	0	1473.474	3208.47
5	383.4598	21.22174	0	1352.016	3126.305
6	404.7745	21.39565	-40	5896.937	2580.919
7	427.4991	21.56957	0	4827.696	3844.428
8	444.0683	21.74348	0	4769.37	4115.132
9	468.0734	21.91739	0	1388.581	4056.806
10	482.6532	22.0913	0	1303.929	3957.429
11	493.0855	22.26522	0	1212.78	3872.777
12	502.4597	22.43913	0	1095.958	3781.628
13	513.4134	22.61304	-15	2036.482	3512.287
14	534.2135	22.78696	0	1309.096	3858.899
15	550.8721	22.96087	0	615.6498	3740.837
16	560.9004	23.13478	0	546.4835	3641.303

17	567.5393	23.3087	0	488.9168	3572.137
18	573.0169	23.48261	0	433.7196	3442.549
19	578.0229	23.65652	0	284.0474	3387.352
20	582.6322	23.83043	0	226.189	3334.294
21	587.7007	24.00435	0	106.9101	3276.436
22	592.3187	24.17826	0	1800.606	1255.01
23	588.4074	24.35217	0	1696.269	981.6916
24	584.6402	24.52609	0	1613.9	877.3542
25	575.9648	24.7	0	1485.016	794.986

Table A-3 Summary Table for VDU

Stage	Temperature (F)	Pressure (psia)	Heat duty (MMBtu/hr)	Liquid flow (lbmol/hr)	Vapor flow (lbmol/hr)
1	149.9999	1.160206	-42.5131	1136.961	1113.469
2	352.2586	1.19888	0	1553.258	1374.232
3	509.1846	1.237554	-80	2542.051	1790.528
4	572.1362	1.276227	0	2324.454	2745.843
5	703.0909	1.314901	0	6.372361	2528.246
6	714.4136	1.353574	0	254.1546	1218.263

Tables A-4, A-5 and A-6 show the material stream results for Preflash, CDU and VDU respectively.

Table A-4 Material Stream Results for Preflash

	MIXCRUDE	PF-STEAM	CDU-FEED	LIGHTS	PF-WATER	NAPTHA
Temperature F	200	400	442.1	170	170	170
Pressure psia	60	60	44.7	39.7	39.7	39.7
Mass Flow lb/hr	1245244	5000	1037845	31031.7	3993.6	177373.1
Enthalpy MMBtu/hr	-963.9	-28.2	-644.3	-36.4	-26.9	-146.9
Vapor Frac	0.01	1	0	1	0	0
Average MW	201.9	18	268.2	50.9	18	101.6
Liq Vol 60F bbl/day						
WATER	80	343	20.2	112.9	274	15.9
METHA-01	180.1		0.3	174.5		5.3
ETHAN-01	430.2		1.4	382.2		46.6
PROPA-01	580.3		7.4	422.4		150.5
ISOBU-01	880.4		24.8	493.8		361.9
N-BUT-01	1120.5		39.1	549		532.5
2-MET-01	640.3		40.5	204.4		395.3
N-PEN-01	2341		175	624.4		1541.7
PC120F	407.6		38.4	81.1		288
PC138F	1101.6		123.1	172.2		806.3

PC163F	1206		171.1	129.7		905.2
PC188F	1309.5		237.8	92.5		979.2
PC213F	1541.2		352.3	69		1119.9
PC238F	2088.3		591.8	56		1440.5
PC263F	3021.2		1040.1	47.6		1933.6
PC287F	2940.1		1209.3	26.8		1704
PC312F	2400.7		1177.2	11.5		1212
PC338F	2368.6		1365.3	5.6		997.7
PC363F	2430.9		1612.1	2.7		816.2
PC388F	2622.5		1961.9	1.3		659.4
PC413F	3076.8		2596.1	0.5		480.2
PC438F	3482.5		3315.1	0.1		167.4
PC462F	3276.9		3263.3	< 0.1		13.6
PC487F	3063.5		3063	< 0.1		0.5
PC512F	2947.5		2947.5	< 0.1		< 0.1
PC537F	2759.6		2759.6	< 0.1		< 0.1
PC562F	2550		2550	< 0.1		< 0.1
PC587F	2413		2413	< 0.1		< 0.1
PC612F	2361.4		2361.4	< 0.1		< 0.1
PC638F	2378.7		2378.7	< 0.1		< 0.1
PC662F	2408.9		2408.9	< 0.1		< 0.1
PC687F	2404.2		2404.2	< 0.1		< 0.1
PC712F	2400.3		2400.3	< 0.1		< 0.1
PC738F	2397.3		2397.3	< 0.1		< 0.1
PC763F	2759.5		2759.5	< 0.1		< 0.1
PC787F	2895.6		2895.6	< 0.1		< 0.1
PC823F	3943.7		3943.7	< 0.1		< 0.1
PC874F	2853.3		2853.3	< 0.1		< 0.1
PC924F	2434.2		2434.2	< 0.1		< 0.1
PC975F	2141.2		2141.2	< 0.1		< 0.1
PC1025F	1997.1		1997.1	< 0.1		< 0.1
PC1075F	1870		1870	< 0.1		< 0.1
PC1125F	1722.9		1722.9	< 0.1		< 0.1
PC1174F	1552.3		1552.3	< 0.1		< 0.1
PC1248F	2520.4		2520.4	< 0.1		< 0.1
PC1349F	2144.6		2144.6	< 0.1		< 0.1
PC1459F	2088.5		2088.5	< 0.1		< 0.1
PC1585F	1465.2		1465.2	< 0.1		< 0.1
*** DRY TOTAL ***						
Liq Vol 60F bbl/day	99920		79815.4	3547.2		16557.4
API Gravity	34.1		27.1	117.3		61.2
Gravity 60F	0.854		0.892	0.569		0.734
Watson UOP-K	11.3		11.4	13.7		12

TBP Curve F						
0%	-98.7		139.8	-300		-81.4
5%	96.9		298.6	-210		30.9
10%	196.1		371.3	-131.5		87.6
30%	402.9		512.9	-4.1		173.3
50%	566.9		671.7	33.8		245.3
70%	771.8		833.8	94.6		290.6
90%	1143.4		1209.3	167.4		364.9
95%	1331.4		1379.1	216.4		393.9
100%	1565.6		1580.2	286.5		425.8
D86 Curve F						
0%	5.2		210.9	-210.1		18.4
5%	145.8		325.6	-133.8		99.7
10%	226.8		381.8	-89.7		139.3
30%	407.9		508.9	20.4		198.8
50%	559.1		655.3	43.8		250.7
70%	741.5		806.9	89.4		282.6
90%	1020.6		1088.1	152.5		347.2
95%	1169.6		1220.3	201.4		375
100%	1318.7		1352.4	250.4		402.8
D1160 Curve F						
0%	-204.2		-19.9	-313.4		-158.4
5%	-72.2		98.3	-254.2		-86.9
10%	20.8		162.5	-216.2		-50.1
30%	182.9		272.6	-129.4		7.2
50%	314.3		402.3	-106.5		55.2
70%	488.2		542.2	-60.6		90.7
90%	822.8		884.9	-5.1		149.6
95%	1002.4		1049.1	32.7		172.9
100%	1236.5		1251.5	87.5		198.6
SULFUR percent	2.436		2.884	0.008		0.214

Table A-5 Material Stream Results for CDU

	CDU-FEED	DU-STM	DU-STM1	DU-STM2	DU-STM3	RED-CRD	DU-WATER	H-NAPTHA	KEROSENE	DIESEL	AGO
Temperature F	442.1	400	400	400	400	576	176.2	176.2	372.2	490.5	531.7
Pressure psia	44.7	60	60	60	60	24.7	15.7	15.7	21.2	22.4	23.3
Mass Flow lb/hr	1037845	12000	3300	1000	800	623640.6	17134.4	83120.8	194379.7	117025.1	19644.8
Enthalpy MMBtu/hr	-644.3	-67.6	-18.6	-5.6	-4.5	-349.3	-115.2	-62.9	-118.8	-67.7	-11.5
Vapor Frac	0	1	1	1	1	0	0	0	0	0	0
Average MW	268.2	18	18	18	18	420	18	118.5	176.8	228.4	284.7
Liq Vol 60F bbl/day											
WATER	20.2	823.3	226.4	68.6	54.9	0.8	1175.5	7.2	8.8	1	0.1
METHA-01	0.3					< 0.1		0.3	< 0.1	< 0.1	< 0.1
ETHAN-01	1.4					< 0.1		1.4	< 0.1	< 0.1	< 0.1
PROPA-01	7.4					< 0.1		7.4	< 0.1	< 0.1	< 0.1
ISOBU-01	24.8					< 0.1		24.8	< 0.1	< 0.1	< 0.1
N-BUT-01	39.1					< 0.1		39.1	< 0.1	< 0.1	< 0.1
2-MET-01	40.5					< 0.1		40.5	< 0.1	< 0.1	< 0.1
N-PEN-01	175					< 0.1		174.9	< 0.1	< 0.1	< 0.1
PC120F	38.4					< 0.1		38.4	< 0.1	< 0.1	< 0.1
PC138F	123.1					< 0.1		123	< 0.1	< 0.1	< 0.1
PC163F	171.1					< 0.1		170.9	0.2	< 0.1	< 0.1
PC188F	237.8					< 0.1		237.1	0.6	0.1	< 0.1
PC213F	352.3					< 0.1		349.7	2.3	0.2	< 0.1
PC238F	591.8					< 0.1		581.8	9.2	0.8	< 0.1
PC263F	1040.1					< 0.1		1003.5	34.2	2.4	< 0.1

PC287F	1209.3					0.1		1127.7	76.6	4.9	0.1
PC312F	1177.2					0.3		1023.8	144.4	8.6	0.1
PC338F	1365.3					0.7		1015.6	331.4	17.4	0.3
PC363F	1612.1					1.9		814	760.7	34.8	0.6
PC388F	1961.9					5.3		410.5	1476.9	68	1.2
PC413F	2596.1					16.1		123.2	2313	140.9	2.9
PC438F	3315.1					46.2		25.8	2961.6	275.1	6.4
PC462F	3263.3					96.6		3.5	2741.1	411.4	10.8
PC487F	3063					180.3		0.4	2266.2	599.2	16.9
PC512F	2947.5					319.3		< 0.1	1680.6	921.1	26.5
PC537F	2759.6					503.5		< 0.1	885.4	1331.9	38.8
PC562F	2550					698.4		< 0.1	271.9	1526.2	53.4
PC587F	2413					905.5		< 0.1	51.8	1382.5	73.2
PC612F	2361.4					1144.7		< 0.1	7.1	1103.9	105.6
PC638F	2378.7					1417.7		< 0.1	0.8	794.9	165.3
PC662F	2408.9					1677.4		< 0.1	0.1	476.8	254.6
PC687F	2404.2					1894.2		< 0.1	< 0.1	196.1	313.9
PC712F	2400.3					2101.2		< 0.1	< 0.1	43.2	255.8
PC738F	2397.3					2261.1		< 0.1	< 0.1	5.1	131.1
PC763F	2759.5					2706.9		< 0.1	< 0.1	0.4	52.2
PC787F	2895.6					2880.4		< 0.1	< 0.1	< 0.1	15.2
PC823F	3943.7					3941.1		< 0.1	< 0.1	< 0.1	2.5
PC874F	2853.3					2853.3		< 0.1	< 0.1	< 0.1	0.1
PC924F	2434.2					2434.2		< 0.1	< 0.1	< 0.1	< 0.1
PC975F	2141.2					2141.2		< 0.1	< 0.1	< 0.1	< 0.1
PC1025F	1997.1					1997.1		< 0.1	< 0.1	< 0.1	< 0.1
PC1075F	1870					1870		< 0.1	< 0.1	< 0.1	< 0.1

PC1125F	1722.9					1722.9		< 0.1	< 0.1	< 0.1	< 0.1
PC1174F	1552.3					1552.3		< 0.1	< 0.1	< 0.1	< 0.1
PC1248F	2520.4					2520.4		< 0.1	< 0.1	< 0.1	< 0.1
PC1349F	2144.6					2144.6		< 0.1	< 0.1	< 0.1	< 0.1
PC1459F	2088.5					2088.5		< 0.1	< 0.1	< 0.1	< 0.1
PC1585F	1465.2					1465.2		< 0.1	< 0.1	< 0.1	< 0.1
*** DRY TOTAL ***											
Liq Vol 60F bbl/day	79815.4					45588.7		7337.3	16016.2	9345.8	1527.5
API Gravity	27.1					19.3		50.8	38.5	33.2	28.9
Gravity 60F	0.892					0.939		0.776	0.832	0.859	0.882
Watson UOP-K	11.4					11.6		11.7	11.6	11.7	11.7
TBP Curve F											
0%	139.8					483.2		27.1	285.3	358.8	434.5
5%	298.6					586.2		133.2	356.6	442.5	531.5
10%	371.3					636.3		187.1	379	472.3	571.9
30%	512.9					753.7		260.8	421.4	530.5	643.3
50%	671.7					850.8		294.2	449.4	563.9	675
70%	833.8					1042.1		329.5	479	597	700.2
90%	1209.3					1352		369.7	519	643.4	733.8
95%	1379.1					1473.3		387.1	536.4	663.4	749.2
100%	1580.2					1604.5		418.8	567.8	698.6	783.5
D86 Curve F											
0%	210.9					527.5		116.3	347.4	424.9	497.9
5%	325.6					603		193.8	390.1	478.5	564.8
10%	381.8					635.6		230	408	501.3	593.5
30%	508.9					732.9		277.8	431.3	536	639.3

50%	655.3					811.3		298	447.7	556.3	658.3
70%	806.9					985.6		321.9	467.2	578.4	674.5
90%	1088.1					1229.9		352.4	497.6	614.7	699.2
95%	1220.3					1322.9		375	520	640	722
100%	1352.4					1416		397.6	542.4	665.3	744.8
D1160 Curve F											
0%	-19.9					276		-77.2	124.2	186.3	244.3
5%	98.3					352.3		-9.4	158.6	231.4	305.8
10%	162.5					386		23	171.6	249	331.5
30%	272.6					479.9		72.4	199.6	289.4	383.4
50%	402.3					557.1		93.6	217.7	311.8	405.1
70%	542.2					729		121.5	241.9	339.3	426.6
90%	884.9					1022.5		153.5	274.7	378.4	455.4
95%	1049.1					1142.8		167.4	289	395.3	468.6
100%	1251.5					1276.7		192.9	315	425.2	498.3
SULFUR percent	2.884					3.764		0.29	1.565	2.247	2.733

Table A-6 Material Stream Results for VDU

	RED-CRD	VDU-STM	RESIDUE	DIST	L-VGO	H-VGO
Temperature F	576	400	714.4	150	352.3	572.1
Pressure psia	24.7	60	1.4	1.2	1.2	1.3
Mass Flow lb/hr	623640.6	20000	191166.9	20542.6	200303.8	231627.3
Enthalpy MMBtu/hr	-349.3	-112.7	-91.7	-115.1	-139	-130.4
Vapor Frac	0	1	0	1	0	0
Average MW	420	18	752.2	18.4	295.8	420.8
Liq Vol 60F bbl/day						
WATER	0.8	1372.1	< 0.1	1372.5	0.4	< 0.1
METHA-01	< 0.1		< 0.1	< 0.1	< 0.1	< 0.1
ETHAN-01	< 0.1		< 0.1	< 0.1	< 0.1	< 0.1
PROPA-01	< 0.1		< 0.1	< 0.1	< 0.1	< 0.1
ISOBU-01	< 0.1		< 0.1	< 0.1	< 0.1	< 0.1
N-BUT-01	< 0.1		< 0.1	< 0.1	< 0.1	< 0.1
2-MET-01	< 0.1		< 0.1	< 0.1	< 0.1	< 0.1
N-PEN-01	< 0.1		< 0.1	< 0.1	< 0.1	< 0.1
PC120F	< 0.1		< 0.1	< 0.1	< 0.1	< 0.1
PC138F	< 0.1		< 0.1	< 0.1	< 0.1	< 0.1
PC163F	< 0.1		< 0.1	< 0.1	< 0.1	< 0.1
PC188F	< 0.1		< 0.1	< 0.1	< 0.1	< 0.1
PC213F	< 0.1		< 0.1	< 0.1	< 0.1	< 0.1
PC238F	< 0.1		< 0.1	< 0.1	< 0.1	< 0.1
PC263F	< 0.1		< 0.1	< 0.1	< 0.1	< 0.1
PC287F	0.1		< 0.1	0.1	< 0.1	< 0.1
PC312F	0.3		< 0.1	0.2	< 0.1	< 0.1
PC338F	0.7		< 0.1	0.6	0.1	< 0.1
PC363F	1.9		< 0.1	1.5	0.4	< 0.1
PC388F	5.3		< 0.1	3.2	2.1	< 0.1
PC413F	16.1		< 0.1	6.2	9.8	0.1
PC438F	46.2		< 0.1	9.3	36.7	0.2
PC462F	96.6		< 0.1	8.5	87.6	0.5
PC487F	180.3		< 0.1	6	173	1.3
PC512F	319.3		< 0.1	3.8	312.5	3.1
PC537F	503.5		< 0.1	2.1	494.8	6.6
PC562F	698.4		< 0.1	1.2	684.6	12.6
PC587F	905.5		< 0.1	0.8	881.7	22.9
PC612F	1144.7		0.1	0.4	1102.1	42.2
PC638F	1417.7		0.2	0.2	1338.4	79
PC662F	1677.4		0.3	0.1	1535	142
PC687F	1894.2		0.6	< 0.1	1650.4	243.2
PC712F	2101.2		1.1	< 0.1	1683.5	416.7

PC738F	2261.1		1.9	< 0.1	1572.9	686.4
PC763F	2706.9		3.7	< 0.1	1493.1	1210
PC787F	2880.4		6.4	< 0.1	1147.6	1726.4
PC823F	3941.1		21.5	< 0.1	892.6	3027.1
PC874F	2853.3		55.6	< 0.1	252.1	2545.6
PC924F	2434.2		138.5	< 0.1	75.2	2220.4
PC975F	2141.2		318.9	< 0.1	21.1	1801.3
PC1025F	1997.1		644.9	< 0.1	5.4	1346.8
PC1075F	1870		1030.5	< 0.1	1.1	838.3
PC1125F	1722.9		1308	< 0.1	0.2	414.7
PC1174F	1552.3		1390.5	< 0.1	< 0.1	161.8
PC1248F	2520.4		2471	< 0.1	< 0.1	49.3
PC1349F	2144.6		2143	< 0.1	< 0.1	1.6
PC1459F	2088.5		2088.5	< 0.1	< 0.1	< 0.1
PC1585F	1465.2		1465.2	< 0.1	< 0.1	< 0.1
*** DRY TOTAL ***						
Liq Vol 60F bbl/day	45588.7		13090.4	44.1	15454.1	17000
API Gravity	19.3		9.7	38.2	27.6	19.9
Gravity 60F	0.939		1.002	0.834	0.889	0.935
Watson UOP-K	11.6		11.7	11.6	11.7	11.6
TBP Curve F						
0%	483.2		876.3	304.2	458.1	621.6
5%	586.2		1007.5	370.2	532.2	717.8
10%	636.3		1054.5	390.5	565.5	749.9
30%	753.7		1163.5	428.3	640.9	807.4
50%	850.8		1263.6	452.5	691.2	866.5
70%	1042.1		1382.2	480.1	738.1	938.9
90%	1352		1526.2	528.9	793.8	1041.7
95%	1473.3		1595.5	558.6	824.7	1086.5
100%	1604.5		1667.6	614	885.6	1156.8
D86 Curve F						
0%	527.5		845.9	362	519	661.8
5%	603		935.6	400.5	569.5	723.9
10%	635.6		974.1	416.4	590.6	750
30%	732.9		1060.7	436.7	640	784.3
50%	811.3		1142.6	450.7	672.8	824.5
70%	985.6		1250.6	468.7	706.1	881.3
90%	1229.9		1389.4	507.2	751.4	976.8
95%	1322.9		1445.7	544.7	791.3	1024.5
100%	1416		1502	582.2	831.2	1072.2
D1160 Curve F						
0%	276		591.1	136.9	269.4	401.1
5%	352.3		703.3	168.2	311.5	460.6
10%	386		753.2	179.8	328.1	484.3

30%	479.9		848.3	204.6	383.2	526.7
50%	557.1		936.8	220.2	418.9	571
70%	729		1052.1	242.7	459.1	635.4
90%	1022.5		1196.3	282.7	507.2	728.6
95%	1142.8		1267.3	307.4	534.2	769.8
100%	1276.7		1342.3	353.6	587.9	835.3
SULFUR percent	3.764		4.822	1.624	2.864	3.675