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Permanent: No 43 Jalan Tropika 5
Address : Taman Tropika, Sg Tangkas
: Kajang, Selangor Darul Ehsan

Name of Supervisor:
Dr. Shuhaimi B Mahadzir

Date: 14/7/09

Date: 14/7/09

DR SHUHAIMI MAHADZIR
Head of Chemical Engineering Department
Universiti Teknologi PETRONAS

APPROVAL PAGE

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Approval by Supervisor (s)

The undersigned certify that they have read, and recommend to The Postgraduate Studies Programme for acceptance, a thesis entitled "**Prediction the individual component distillation curves of the blended feed using a hybrid GDM-PcLE method**" submitted by **Mohd Rosdi Naim Bin Mat** for the fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.

14/07/09

Date

Signature

:



Main Supervisor

:

Dr. Shuhaimi b Mahadzir

Date

:

14/7/09

Co-Supervisor 1

:

-

Date

:

-

TITLE PAGE

UNIVERSITI TEKNOLOGI PETRONAS

**Prediction the individual component distillation curves of the blended feed
using a hybrid GDM-PcLE method**

By

Mohd Rosdi Naim b. Mat

A THESIS

SUBMITTED TO THE POSTGRADUATE STUDIES PROGRAMME

**AS A REQUIREMENT FOR THE
DEGREE OF MASTER OF SCIENCE
IN CHEMICAL ENGINEERING**


BANDAR SERI ISKANDAR

PERAK

JUNE, 2009

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTP or other institutions.

Signature :  _____
Name : MOHD ROSDI NAIM B. MAT
Date : 14/02/19

ABSTRACT

A comprehensive knowledge of the properties and characterisations of the individual component in the blended feed is primary importance because different feedstock blending yields different products palate. Crude oil / condensate distillation unit optimization is an uphill task because unavailability of cheaper and reliable on line feed and product analyzers. Furthermore, laboratory analysis for feedstock characterization is very costly and time consuming. Alternatively, feed synthesis technique is used to reconcile the entire range of feed distillation curves by back blending the product streams from the actual column operation. The TBP and SG correlation are widely been used to estimate other bulk properties because they give the most accurate results. Due to highly nonlinear behaviour, methods like linear regression, non linear regression and rigorous models are adopted to predict TBP and SG distillation curves. The latter could give better accuracy results, but it is more complex, lengthy and costly to be implemented. In addition, the rigorous model commercially available such as PetrosimTM and Hysis 3.1TM are only being used to predict blended feed distillation curves, not for the individual component. Thus, a hybrid approach is proposed to overcome the deficiency of current methods and practices. The proposed method integrates the most versatile General Distribution Model (GDM) with a Pseudo-component Linear Equation (PcLE) method to predict the entire range individual component TBP and SG distillation curves of the blended feed from the readily available plant data, which are routinely taken by refiners. The predicted results given by hybrid GDM-PcLE model are almost agreeable with the lab results. A case study using the proposed short cut feed synthesis procedure and hybrid GDM-PcLE model showed additional 5% Naphtha yield can be achieved by changing the current feed blending ratio and product cut points. The accuracy of the predicting results can be improved if the distillates samples are to be carried out simultaneously and the flow meters are calibrated and corrected the measurements to density and temperature of the measuring devices. Since PcLE method is simple and open application, it can be easily integrated with iCONTM to enhance its application predicting the pure component TBP and other distillation curves from blended feed.

ABSTRAK

Pengetahuan yang komprehensif terhadap sifat-sifat dan karektor bagi komponen-komponen individu dalam campuran suapan adalah sangat mustahak kerana campuran bahan mentah yang berbeza akan menghasilkan “palate” produk-produk yang berbeza. Pengoptimuman unit penyulingan adalah sangat sukar disebabkan ketiadaan penganalisis secara “on line” yang murah dan berwibawa. Disamping itu juga, analisa makmal sangat mahal and memakan masa. Sebagai alteratif, teknik sintesis suapan digunakan untuk membina keseluruhan lengkung takat didih tulen (TBP) dan graviti-tentu (SG), dengan cantuman semula produk-produk sulingan pada operasi sebenar turus. Korelasi TBP dan SG digunakan secara meluas bagi meramal sifat-sifat suapan yang lain kerana ramalannya adalah yang paling tepat. Disebabkan lengkung data suapan yang tidak linear, ia selalunya diramal menggunakan kaedah regresi linear, tidak linear dan model “rigorous”. Ramalan melalui model “rigorous” ini agak tepat, tetapi ianya terlalu kompleks, memakan masa dan mahal. Di samping itu, model “rigorous” yang dikomersialkan seperti PetrosimTM and Hysis 3.1TM hanya meramal lengkungan bagi campuran suapan sahaja, tetapi tidak untuk komponen-komponen individu dalam campuran suapan tersebut. Oleh itu, pendekatan “hybrid” dicadangkan bagi mengatasi kelemahan amalan sediaada melalui pengabungan Model Taburan Am (GDM) yang “versatile” dengan kaedah Persamaan Linear Komponen Palsu (PcLE), menggunakan data maklumat sediaada yang direkodkan secara rutin, Melalui kaedah ini, ramalan bagi lengkung takat didih hasil pemeluwapan dan taburan graviti didapati hampir sepadan dengan hasil analisa makmal. Kajian kes yang dijalankan menggunakan prosedur baru yang lebih ringkas menunjukkan hasil perolehan Naphtha dapat ditingkatkan lagi sebanyak 5% dengan menukar nisbah campuran suapan semasa dan titik potong produk. Ketepatan ramalan melalui kaedah ini dapat ditingkatkan sekiranya sampel produk-produk sulingan diambil secara serentak dan meter alir di tentuukur dan dibetulkan mengikut ketumpatan dan suhu peranti ukur. Oleh kerana kaedah PcLE ini mudah dan aplikasinya terbuka, maka mudah untuknya diintegrasikan dengan iCONTM bagi menambah-baikkan aplikasi sediaada supaya dapat meramal lengkung takat didih dan taburan graviti bagi komponen individu yang terdapat dalam campuran suapan.

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DEDICATION

This work is dedicated to
My beloved wife, Faizah Md Yasin and daughters
My mother, Habshah Abd Hamid and late father, Mat Endut
My brothers and sisters

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ABBREVIATIONS

ASTM	American Society for Testing Material
EFV	equilibrium flash vaporization
IBP	initial boiling point
FBP	final boiling point
HN	Heavy Naphtha
CH	Carbon-to-hydrogen weight ratio
WTR	weight transfer ratio
VABP	volume average boiling point
MABP	molar average boiling point
WABP	weight average boiling point
CABP	cubic average boiling point
MeABP	mean average boiling point
MTHS	Molecular-type homologous series matrix
MEPP	Molecularly Explicit Property Prediction Mode
GDM	General Distribution Method
NCM	Narrow Cut Method (NCM)
SD	simulated distillation
CDU	Crude distillation unit
CFU	Condensate fractionation unit
LP	Linear Programming
PcLE	Pseudo-component Linear Equation
GC	Gas Chromatograph
AD	absolute deviation
AAD	average absolute deviation

NOMENCLATURES

α	blending ratio in %
P	bulk property (e.g. T_b , K_{vis} and etc.)
P_o	property at IBP
P_{ij}	bulk property of pure condensate j of i^{th} pseudo-component
ν	viscosity (cst)
K_{vis}	Kinematic viscosity
RVP	Reid Vapor Pressure
KW	Watson factor
MW	molecular weight
SG	standard specific gravity
$P_{\text{vap } i}$	vapour pressure
T	temperature
T_b	boiling point
T_c	critical temperature
P_c	critical pressure
V_c	critical volume
ω	acentric factor
$^{\circ}\text{F}$	degree Fahrenheit
$^{\circ}\text{C}$	degree Celsius
x	volume or mass fraction
x_c	cumulative volume fraction
x'_c	discrete cumulative fraction
W	weight in criterion
I	Refractive index
θ	characteristic property (temperature independent property)
R^2	deviation co-efficient of parity plot
E^2_p	overall error square of the mixture bulk properties

CHAPTER I

INTRODUCTION

1.1. Overview of modern refinery complex

Petroleum refining is unique, in the sense that each plant has its own unique arrangement and combination of refining processes, that determined by the refinery location, desired products and economic considerations. There are most probably no two refineries that are identical in every respect. Generally, refining processes are classified into three main process namely; separation, conversion and finishing. Refineries nowadays are built with complex processing schemes having a combination of various technologies for heavy ends upgrading, product quality improvement, efficient fuel usage and controlled refinery emissions. Modern refineries mostly perform the seven basic operations as listed in table 1.1 (Hsu and Robinson, 2006):

Table.1.1 Basic operations in modern refinery

Separation	<ul style="list-style-type: none"> • Distillation • Solvent refining 	Combination	<ul style="list-style-type: none"> • Catalytic polymerization • Alkylation
Conversion	<ul style="list-style-type: none"> • Carbon removal • Hydrogen addition 	Treating, Finishing & Blending	<ul style="list-style-type: none"> • Gasoline, Kero and diesel • Lubes and waxes • Asphalt
Reforming	<ul style="list-style-type: none"> • Catalytic reforming • Steam/hydrocarbon reforming 	Protecting the environment	<ul style="list-style-type: none"> • Waste water treatment • Disposal solid • Sulphur recovery
Rearrangement	<ul style="list-style-type: none"> • Isomerisation 		

A typical modern refinery complex and distillation unit are shown in Figure 1.1a and (b) below. Figure 1.1a shows overall scheme of modern refinery that covers various unit processes and the flow of intermediate product streams that occurs between the inlet crude oil feedstock and the final end products. Figure 1.1b shows a simplified flow scheme of crude distillation unit, comprises of atmospheric and vacuum distillation column and their respectively distillation products.

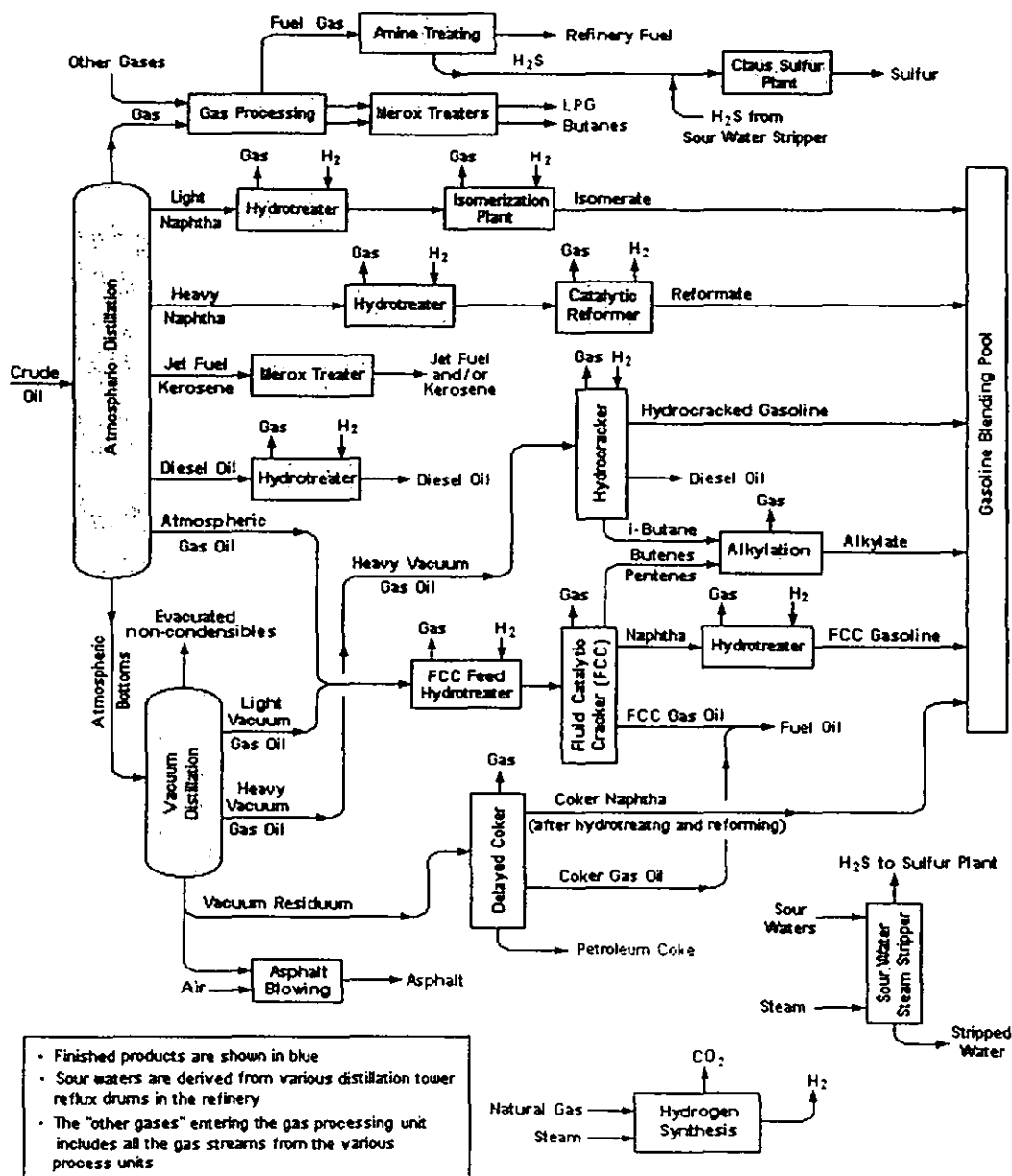


Figure 1.1a Example of process flow scheme for a typical modern refinery complex

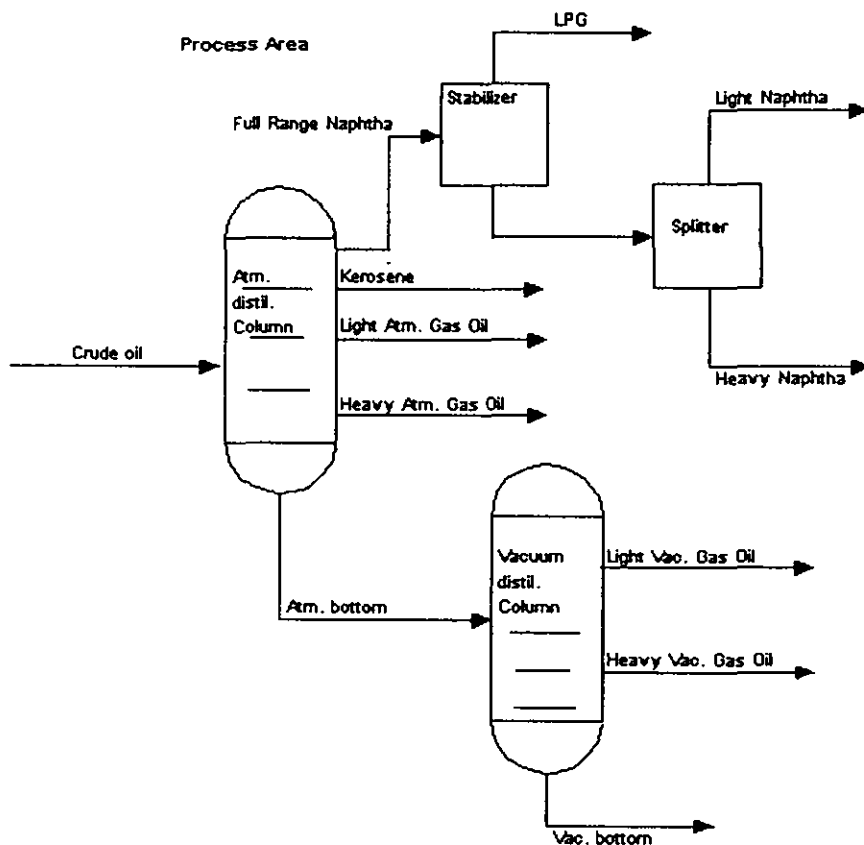


Figure 1.1b Simplified flow scheme of distillation unit

1.2. Distillation unit

The distillation unit of refinery can be either Crude Distillation Unit (CDU) or Condensate Fractionation Unit (CFU) depending on the feedstock. Some refineries are having both of them. They are the first unit that processes petroleum in any refineries regardless of their complexity. The unit separates crude oils and / or condensates into several petroleum fractions according to boiling ranges. Examples of distilled fractions are naphtha, kerosene, diesel and heavy gas oil. The boiling ranges of typical crude oil fractions are shown in Table 1.2, (Parkash, 2003).

Table.1.2 Typical boiling ranges for crude oil fractions

Fraction	Boiling point	
	Boiling ranges, °F	Boiling ranges, °C
LPG & light gases	< 90	< 32
Light Naphtha	90 – 190	32 – 87
Heavy Naphtha	190 – 380	87 - 193
Kerosene	380 – 520	193 – 271
Light gas Oil (LGO)	520 - 610	271 – 321
Atmospheric Gas Oil (AGO)	610 - 800	321 – 427
Vacuum gas oil (VGO)	800 - 1050	427 - 565

The actual cut point target within the above range for each distillate products is selected upon downstream processing objectives and product specifications. The temperature at any point on the TBP-cumulative yield (vol%) curve represents the true boiling point of the hydrocarbon material present at the given volume percent point distilled. A typical TBP curve of crude and products are shown in Figure 1.2 below.

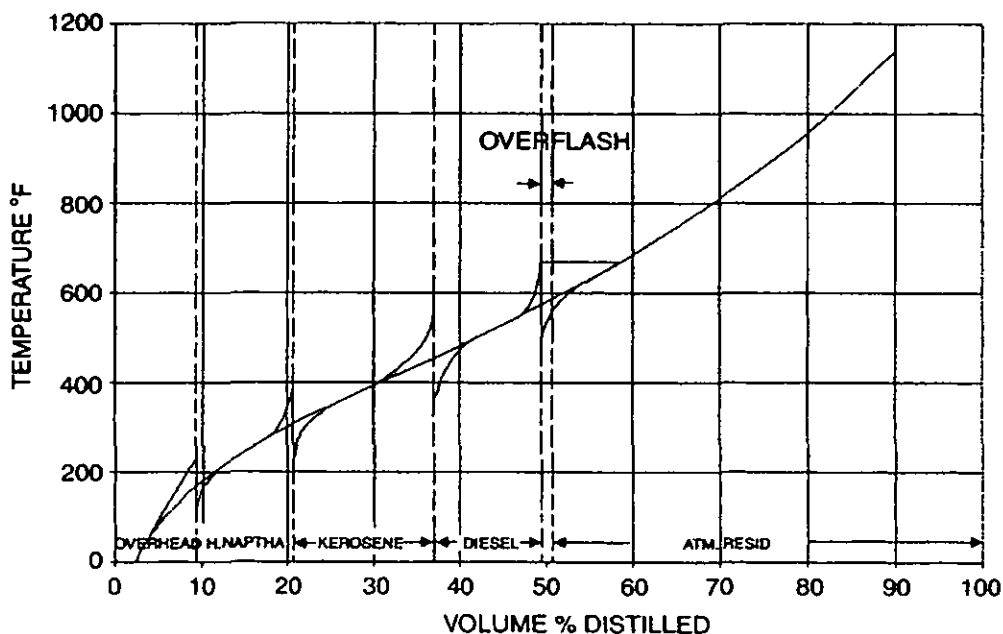


Figure 1.2 Feed TBP curve and petroleum fractions of atmosphere distillation tower

The major factors that drive the entire crude processing and secondary unit operations of refinery plant are product demands, qualities and prices. The selections of feed stocks to distillation unit (CDU and / or CFU) are of primary importance. This is due to the fact that, different crude oils or condensates would yield different palate of optimum products. For example, the multiple streams with multiple blend options resulting in different grades of a product, and hence making the task of refinery planning cumbersome and demanding. Therefore a comprehensive knowledge of feed stocks properties and characteristics is essential for refiners to determine the optimum process operating conditions for the distillation columns of CDU and CFU that maximise the distillate product yields, and at the same time meets the downstream processes specifications.

On the same note, feed analysis and characterisations are extremely important because any deviation in their properties would affect the qualities and specifications of the distillate products. The deviation of feed bulk properties is very likely due to several factors like stratification in the reservoirs, contamination and feeds pre-mixing during transportation and storage (Parkash, 2003).

1.3. Crude oil and condensate characterisation

Crude oil, condensates and petroleum fractions of the distillation unit products are complex mixtures of hydrocarbons. Determining the exact composition of crude oils and heavy condensates is not feasible. Instead it is sufficient to characterize them in terms of certain gross or bulk properties such as Reid Vapor Pressure (RVP), Flash Point and Pour Point for heavy distillate.

Generally, crude oil and condensate are defined by assays using boiling curve analysis. Other properties, such as molecular weight (MW), specific gravity (SG), and viscosity, may also be determined at specific cumulative volume percentages. All these properties are defined as crude or condensate distillation curves. SG and MW are commonly supplied as "bulk properties" which are measured for the overall oil sample. These boiling curve measurements and bulk properties are then related to the physical properties of the oil or condensate using correlations. The basic

characterisation parameters are important to determine the specifications of end products. For example Reid Vapor Pressure (RVP) for volatile products, Flash Point for light distillate, Pour Point and Kinematic Viscosity (K_{vis}) for heavy distillate. The properties of crude oil and distillate products are usually measured in laboratory using standard procedures. The prominent organisation that correlates and standardise the methods for the inspection and evaluation of petroleum and petroleum fraction is the American Society for Testing Material or ASTM (James, 2002).

By using generalised empirical method as defined by Riazi and Daubert's (Riazi, 1980) two parameter equations, other basic characterisation parameters as mentioned above can be determined. The most important and widely used parameters for crude oil and petroleum fraction characterisation are true boiling point (TBP) and SG. The MW and refractive index (I) and carbon-to-hydrogen weight ratio (CH) parameters may be used as other options for prediction of properties of hydrocarbon (Riazi, 2005). The correlations in term of TBP and SG parameters have been reported as the most accurate methods for the estimation of other bulk properties. Most of the correlations used to characterise the petroleum fractions were developed using input parameters from bulk properties where the average boiling point is generally used to determine the single characterizing boiling point.

TBP curve is a graphical depiction of the boiling temperature of a fluid plotted against volume fraction distilled. Riazi (2005) defined in total five commonly used average boiling point (ABP), which is defined as.

$$ABP = \sum_{i=1}^n x_i T_{bi} \dots\dots\dots \text{equation 1.1}$$

where n is number of fractions, x_i is the corresponding fraction of i^{th} pseudo-component in vol%, mol% or wt% and T_{bi} is normal boiling of i^{th} pseudo-component in Kelvin

Three of these average boiling points are volume average boiling points (VABP), molar average boiling points (MABP) and weight average boiling points (WABP). Two other average boiling points, namely, the cubic average boiling points (CABP)

and mean average boiling points (MeABP) are defined in equation 1.2 and equation 1.3, respectively.

$$CABP = \left(\frac{1}{1.8} \right) \left[\sum_{i=1}^n x_{vi} (1.8T_{bi} - 459.67)^{1/3} \right]^3 + 255.37 \dots \text{equation 1.2}$$

$$MeABP = \frac{MABP + CABP}{2} \dots \dots \dots \text{equation 1.3}$$

The above correlations do not characterize the fraction very well for wide boiling range fractions. This is because the mixtures comprise a large number of hydrocarbon compounds which varies along the distillation curve.

Therefore feed stock characterisation is important for CDU and CFU to produce an optimal amount of finished products that meets product quality specifications and to provide an economic assessment for crude oils.

1.4. Method to predict complete distillation curves

It has been impossible to rely on current measurement methods because of large uncertainties and biases, resulting in poor design and specification criteria. In many cases, complete distillation data for the entire range of percent distilled (cumulative yield) is not always available. Various methods and models have been developed by researchers to predict accurately the entire range of distillation curves from available data, for example linear regression, non linear regression and rigorous models. The commonly used technique is feed synthesis by back blending the product streams from actual column operation (<http://www.petro-sim.com>).

1.5. Design and operations optimisation

CDU and CFU are crucial process in the refinery because there are the first units in refinery complex. Accurate and frequent quality predictions of the feed and products run downs would dramatically increase the performance of the distillation tower and

also of the entire refinery downstream processes. However, poorly analysed and predicted feeds properties would decrease the unit performances.

The optimum design and operating parameters are basically referred to maximizing the desired distillate product yields that meet the required specifications at the lowest operating cost within the design margin of the distillation. The main input to process optimisation is distillation data of the pure feed stocks (crude oil or condensates) where the potential yield of distillate products at their boiling ranges can be extracted. Mathematical methods like Linear Programming (LP) allows the current unit operating parameters to be optimised such as by adjusting the feed blending ratio and product cut points. The objective is to maximise profitability while achieving the required properties of the desired product yields. Typical product cut points and the processing use are given in Table 1.3 (Gary et al., 2007)

Table 1.3 TBP cut points for various Crude oil fractions

Cut	IP (°F)	EP (°F)	Processing use
Light Naphtha (LSR)	90	180	Minimum light gasoline
	90	190	Normal LSR method
	80	220	Maximum LSR cut
Heavy Naphtha (HSR)	180	380	Maximum reforming cut
	190	330	Maximum jet fuel operating
	220	330	Minimum reforming cut
Kero	330	520	Maximum kerosene cut
	330	480	Maximum jet 50 cut
LGO	420	610	Maximum diesel fuel
	480	610	Maximum kerosene

1.6. Problem statement

The deviation in feed properties would affect the qualities and specifications of the distillate products which could lead to products give away for final products. In addition, the deviation would have an effect on the performance of downstream process units for intermediate products if the column's operating parameters are not adjusted accordingly. Even though feeds samplings and laboratory analysis to confirm bulk properties are performed frequently, a deviation in feed properties is still possible, especially during online mixing in the pipeline. At present, prediction of TBP curve and bulk properties

distribution in the blended feeds are normally performed using commercial simulation software, for example PetroSIM™ (<http://www.petro-sim.com>). The feed is synthesised using distillate product data through iterative process until the calculated feed data matches with product data. However, the methods and procedures are tedious, time consuming and requires some level of skills and expertise. As is typical in many refineries, the lack of a simple yet accurate method has led them to operate their CDUs and CFUs based on experience or based on operating parameters recommended by consultants during detailed design stage.

1.7. Objectives

The main objective of this study is to develop a simple and less complicated algorithm predicting accurately the individual feed component distillation curves of the blended feed. The proposed method would assist plant engineer exploring and exploiting the flexibility of the distillation column operation in order to maximise the desired product yields.

A simple algorithm is proposed by enhancing the current feed reconciliation procedure using a hybrid modelling method. The hybrid model is basically an integration of General Distribution Model (GDM) with a new technique named as “Pseudo-component Linear Equation, (PcLE)” that able to predict individual feed component distillation curve.

There is a trade-off between accuracy and complexity of the methods used to predict feed distillation curves. A cheaper, simpler and faster method of predicting accurate feed distillation curve is required to fill the technology gap. By adopting optimisation techniques e.g. swing cut methods, these predicted data can be very useful to plant operation engineers to determine the optimum feed blending ratio and effective cut points.

CHAPTER II

LITERATURE REVIEW

2.1 Introduction

Crude oil is not a homogeneous raw material, and has a unique chemical composition that depending on the manner it is been formed. It is reported that currently, more than 150 crude grades are traded in the world market. They are normally classified as paraffin base, naphthalene base, asphalt base, or mixed base (Gary, Handwerk, Kaiser, 2007). A complete and definitive analysis of a crude oil is reported in crude assay where laboratory and testing data that defines the properties of the specific crude are compiled (Parkash, 2003).

The boiling range of the crude gives an indication of the quantities of the various products present. The most useful type of distillation is known as a true boiling point (TBP). However the determination of the yield and properties of the petroleum fractions have always been challenging. Beside the non-linearity of the distillation curve, the crude assays usually provide data on limited number of cuts (Riazi, 2005). Furthermore, most of the distillation data is non linear.

A competitive market, stringent environmental laws and regulations, high crude oil prices, and advancement in process design technology have driven the refineries to deploy process optimisation of unit operations. Refineries are consistently looking for opportunities to save cost through feeds blending. Therefore methods for characterisation and prediction of blend feed's bulk properties are very important for refineries to evaluate the quantity and qualities of the resulting distillate products that can be produced by distillation column.

2.2 Crude oil characterisation

Crude oil characterization is essential to predict physical and thermodynamic properties as well as the type of hydrocarbons present in a refinery feedstock. The predicted feedstock properties can be used for refinery unit operations to produce an

optimal amount of finished products, to meet product quality specifications and to provide an economic assessment for crude oils. The choice of characterisation method and techniques to predict distillation data will strongly influence the predicted results.

There are several correlations between yield and the aromaticity and paraffinicity of crude oils. The most widely used is Watson characterisation factor (K_w). It is an indicator of the paraffinicity of the oil; as such K_w ranges from < 10 for highly aromatic material and to almost 15 for highly paraffinic compounds (Gary, Handwerk and Kaiser, 2007). In addition to that, to model a process containing a crude oil or condensate, the properties of the oil must be known or at least estimated. However, determining the exact composition of crude oils and heavy condensates is not feasible because of the enormous number of components included in these mixtures. But, surprisingly, the chemical compositions of crude oil are uniform even though their physical characteristic varies widely (Gary, Handwerk and Kaiser, 2007).

The characterisation of petroleum fractions and crude oils is dependent on the properties of pure hydrocarbons. Through characterisation, the basic parameters needed for the estimation of various physical and thermodynamic properties maybe estimated. Characterization of petroleum fractions usually involves the use of measurable properties to calculate basic input parameters for thermodynamic correlations. Relatively, simple analytical tests are run on the crude, and the result of these is used with empirical correlations to characterize the crude (Riazi, 2005).

Non-experimental approaches for characterisation of hydrocarbon can be classified into three categories namely; (1) pseudo-component, (2) average structural parameter methods and (3) compound class. The pseudo-component methods use bulk properties in conjunction with distillation data for the entire stream to generate boiling point cuts and their properties. Average structural parameter methods represent petroleum mixtures using the functional groups that present in the components. The method included the ‘‘group contribution method’’ and the ‘‘average molecular parameters’’. Finally, the compound class methods lumps the components containing compounds with similar molecular form to predict the percentage of PNA in an olefin-free petroleum fraction. The examples of these methods are refractivity intercept–density method and Riazi and Daubert correlations (Zhang et al., 2008).

Characterization of petroleum fractions usually involves the use of measurable properties to calculate basic input parameters for thermodynamic correlations. For narrow boiling point range (around 50 – 60°C) and light petroleum fractions, the most commonly available data from laboratory measurements are distillation data (boiling point, T_b) and specific gravity (SG). Petroleum fractions can be considered light ($MW < 300$, or heavy ($MW > 300$). For heavier fractions, where distillation data at atmospheric pressure are usually not available, viscosity or hydrocarbon type analysis are measured (Aladwani et. al., 2005).

For light petroleum fractions, Riazi and Daubert (1980) showed that the physical properties of pure compounds and undefined hydrocarbon mixtures can be predicted using boiling point and specific gravity in an empirical equation of the following form:

$$\theta = aT_b^b SG^c \quad \text{.....equation 2.1}$$

In equation 2.1, T_b is the normal boiling point in absolute degrees (Kelvin or Rankine), SG is specific gravity at 60 °F, and θ is a characteristic property (temperature independent property) such as molecular weight, critical temperature and critical pressure. The prediction accuracy of equation 2.1 is reasonable over the boiling range of 100-850 °F for the following properties: molecular weight, liquid density, liquid molar volume, critical temperature, critical pressure, critical volume, refractive index, heat of vaporization and ideal gas heat capacity.

However, equation 2.1 was developed based on a two-parameter potential energy relation applicable to non-polar compounds; it is therefore not capable to predict properties for polar compounds such as alcohol and water.

Since the prominent parameters for crude oil and petroleum fraction characterisation are TBP and SG because their correlations are the most accurate methods for the estimation of other bulk properties, Riazi et al. (1987) improved the previous technique by dividing any hydrocarbon fraction into an infinite number of components. With known or estimable true boiling point (TBP) and the specific

gravity (SG) along the distillation curve, the technique was used to estimate the properties of heavier fraction hydrocarbon mixtures.

The identification of all actual components present in the crude oil is practically impossible. Therefore, dividing hydrocarbon fraction into several numbers of components to create pseudo-components has been accepted as a convenient approach. The approach has been developed quite as far back in the 1930s and has been used for flash calculations during the early days of computer at the end of 1960. An advantage of the pseudo-component method was that it is the non-iterative characterization procedure. Miquel (1994), has developed a method for characterizing petroleum fractions based on pseudo-component by assuming a constant Watson's characterization factor for all the pseudo-components. The method requires only a TBP curve and the entire fraction's density.

Eckert et al. (2005) highlighted that, even though the pseudo-component method still widely accepted today as a convenient method in the simulation of separation equipment, a number of problems are aroused mainly due to the undefined physical properties of pseudo-components and unreliable empirical methods. For example, the pseudo-component cannot define any chemical character of the components forming the mixture in chemical reactions occurring in the studied processes. Not only that, a pseudo-component is primarily defined only by its (pseudo) boiling point and by some additional parameters, mostly by specific gravity, molecular weight or viscosity. Thus, all other physical properties that needed for simulation calculations must be estimated. Unfortunately, the reliability of common estimation methods for critical properties, the acentric factor, etc. is rather low according to the results of testing published. In addition, pseudo-components cannot use group contribution methods (e.g. UNIFAC) because the method requires information about the molecular structure of compounds in order to estimate some parameters (e.g. binary interaction parameters for vapour-liquid equilibrium). Furthermore, the information about the type of the mixture, e.g. whether paraffinic or aromatic compounds are prevailing, or about the type of some of its important components (e.g. polar compounds) could not be easily utilised. Finally, an arbitrary combination of pseudo-components and compounds identified in the original mixture are not supported in commercial simulation programs. That is, it is not possible to place a real component into the

middle of the temperature range used for the definition of pseudo components without knowing its content.

To overcome the problem, Eckert et al. (2005) proposed a more reliable characterization method for complex mixtures by using real component as substituting mixture. This is because the thermodynamic and transport properties of real components are readily available with high accuracy, thus eliminate all disadvantages adhered by using pseudo-components. The author highlighted that; characterisation of complex mixtures using this new approach is fully acceptable even for simulation calculations of large-scale and complex processes including various mass and heat transfer operations. The method can replace the traditional approach based on the definition of pseudo-components for low and moderate normal boiling points. Although this procedure gives good results when compared with the distillation products of a crude oil mixture, it however has a major limitation if the paraffinic, naphthenic or aromatic contents of the cuts need to be determined. This is due to the fact that, the method relies on the database of real components. As such the higher the number of components in the database, the higher the probability of finding components matching closely with the characterization data. This has made the task to evaluate, analyse and make comparison on each individual solution very tedious due to redundancy of the real components characteristics which required an extensive testing within simulation calculations of a chemical engineering process.

On other development, Juan Gomez-Prado et al. (2008), developed a methodology for the characterisation of crude oil refinery feed stocks and integrated with refinery models to optimise the refining process by increasing its “energy impact” through the production of more efficient and potentially cleaner fuels. In this methodology, a new compound class approach is used to represent any hydrocarbon stream (with boiling range up 700 °C) via a modified molecular-type homologous series (MTHS) matrix. The fraction of each cut in the feedstock stream is estimated by minimising the discrepancies between the bulk physical properties and the ones reconstructed through our characterisation method. Mixture properties are calculated by applying Kay’s mixing rule (Gases and vapours at high temperature and pressure—density) of hydrocarbon. A technique for integrating our characterisation approach with refinery lumped kinetic models is also presented. The MTHS matrix as shown in Figure 2.1 is

used to visualise a petroleum mixture as follows: its rows represent the carbon number (molecular size) and its columns represent the homologous series (e.g. paraffins, naphthenes, aromatics). The entries of the MTHS matrix represent the molecular/weight fraction of each component/lump.

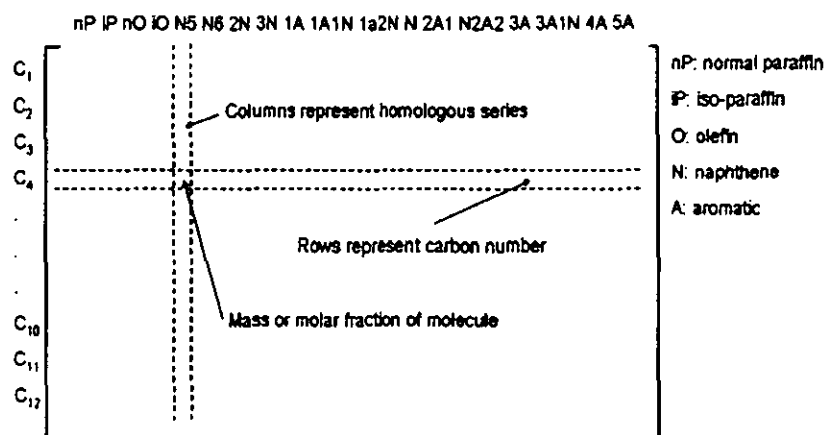


Figure 2.1 Molecular-type homologous series matrix (MTHS).

Beside that, the techniques of sample taken and measured are also important. Thomas (2006) proposed an enhancement approach of the usual distillation curve measurement that allows optimal information content. The author presented several modifications to the measurement of distillation curves. The method minimised uncertainty of temperature and volume measurement and a composition-explicit data channel in addition to the usual temperature–volume relationship. The modification of the temperature–volume relationship is achieved with a new sampling approach that allows precise qualitative as well as quantitative analyses of each fraction. In the new approach, the distillation temperature is measured in two locations, at the usual location i.e. at the bottom of the take-off in the distillation head and also measured directly in the fluid. The programmable temperature controller increases the fluid temperature to achieve a constant mass flow rate of vapor through the distillation head. This approach eliminates the aberrations that one typically encounters in the data due to fluctuations in distillation rate. The analysis is done by gas chromatography coupled with specific or universal detectors. The author claimed that

the modification is the most significant change because the composition is the most important underlying parameter that governs the shape of TBP curve.

2.3 Techniques to predict complete distillation data

The stringent quality requirement of petroleum products in a highly competitive market makes on-line monitoring and control of product properties essential. However, only a few on-line hardware sensors are available and the available sensors are also difficult to maintain. Therefore, methods to predict complete distillation data for petroleum fractions are required to fill in the technology gap. Eckert et al. (2005) stated that non-linear of TBP curve is difficult to predict due to lack of knowledge about the functional form of the underlying equations.

Maples (1997) described the use of linear regression analysis in determining crude properties with variable boiling points. Linear regression analysis was used to simulate seasonal variations in refinery operations and to explore other operating scenarios. Crude assays include a TBP curve, which consists of crude properties given at discrete boiling points. Consecutive fractions are blended together to obtain larger fractions of boiling ranges. However, an engineer simulating different scenarios of refinery operation is interested in blends with different boiling point ranges than those reported from crude assays. Regression analysis allows the engineer to determine the yields and properties of any fraction of crude not provided by the crude assays.

A conventional method to predict the properties fraction is Narrow Cut Method (NCM). The concept is based on pseudo components and iteration calculations (Parkash, 2003). It is also highlighted that linear regression and linear recursion modelling approaches have been widely used to predict TBP curve. The yields and qualities of particular products can be determined by breaking the distillation into narrow cuts called pseudo-components. Moreover the properties of the narrow cuts from the crude assay data can be used to determine the yields and qualities of blended feed.

Ramin et al. (1997) developed a set of conventional feed-forward multilayer neural networks to predict basic properties of pure compounds and petroleum fractions based

on their normal boiling point (T_b) and liquid density at 293 K. The method has been applied to predict critical temperature (T_c), critical pressure (P_c), critical volume (V_c), acentric factor (ω) and molecular weight (MW).

Tirtha et al. (2004) highlighted that the non linear TBP curve and crude composition changed always lead to erroneous property predictions. Poorly predicted properties resulted in poor control action and hence loss of profit because of quality give away. The authors proposed an algorithm that uses the crude TBP curve and other routinely measured variable such as flow rates, temperatures and pressures in the crude distillation unit (CDU) to predict the product properties. The model is developed such that it uses only easily measurable secondary variables as input, is also referred to as 'Soft Sensors' since it serves the same purpose as hardware sensors to provide the properties on-line. In the procedure, the top plate, side-stripper draw plates and flash zone temperatures are measured and corrected for hydrocarbon partial pressures to obtain equilibrium flash vaporization (EFV) temperatures. These product EFVs are converted to product TBPs and are superimposed on the crude TBP curve as illustrated in Figure 2.2.

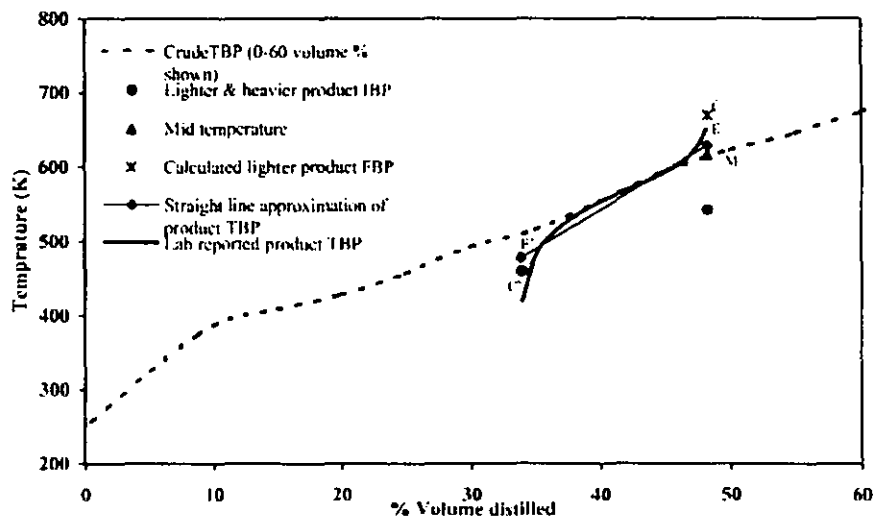


Figure 2.2 Product TBPs is superimposed on the actual crude TBP curve

The procedure assumed that the initial boiling point (IBP) of the next heavier product lies vertically below the final boiling point (FBP) of the product under consideration.

Moreover, the two points are also assumed to be equidistant from the crude TBP curve. A straight line approximation of the product TBP curve is used to obtain intermediate temperatures. These TBP temperatures are converted to product ASTM temperatures which are correlated with the desired product properties.

The existence of steady state has been assumed in the development of the simulator as well as the back calculation procedure and it is, therefore, necessary to ensure that the plant is operating under steady state conditions before proceeding to use these models. The most difficult part of the above technique is to calculate accurately the hydrocarbon partial pressure because as we all know that the pseudo-component is measured base on bulk property.

Riazi (1997) presented a method based on a two-parameter distribution method to predict complete property distributions for a C_{7+} fraction. These properties include MW, TBP, SG and refractive index (I). In this technique, whichever three mixture bulk properties such as molecular weight, specific gravity, and refractive index are needed. For example, if a TBP analysis for the fraction is available, then only two bulk properties such as molecular weight and specific gravity (or refractive index) are sufficient. The author reported that the predicted distributions for various properties are compared with experimental data of some 48 crude samples. The author also claimed that the method is also applied for flash vaporization of a Russian crude oil, and predicted distributions for feed, vapour, and liquid streams are compared with actual data. Sergio et al. (2007) made a comparison of 25 probability distribution functions for distillation data of petroleum fractions and found that the distribution functions with four parameters showed better fitting capability than those with three parameters. Two-parameter functions were not effective in fitting distillation data.

Riazi (1997) developed characterisation of crude oil or C_{7+} fractions using 3 type distribution models to predict the complete distillation curve. These are exponential, gamma and generalised model. Among them, the generalised model is the most versatile distribution model that can be applied to all major characterisation parameters. However, Tareq (2006), claimed that a single value for boiling point or specific gravity does not characterize the fraction very well because the wide boiling range fractions are mixtures of a large number of hydrocarbon compounds which

varies along the distillation curve. In fact the authors highlighted that many existing correlations are based on properties of pure compounds. Therefore errors in predicted values from the correlations increase significantly when the methods are applied to mixtures. Although, the method developed by Riazi is very useful, but it is far from being considered owing to molecularly explicit, and has not proven predictive ability for other properties. To overcome that, the author presented a novel technique to predict the thermo-physical and transport properties of light petroleum fractions using Molecularly Explicit Property Prediction Mode (MEPP) based on the knowledge of their global properties that are easily measured in the laboratory such as ASTM D86 distillation. The technique is based on real-time simulation using simplified correlations. The proposed model is based on the concept that the global properties of a petroleum fraction must be equal to those calculated from the pure components comprising that petroleum fraction. When both bulk and pure component properties are available, the composition of a limited set of pure components in the petroleum fraction may be predicted.

Doug Hyung Lee et al (2006) proposed a new approach to predict TBP curve by using an inferential modelling technique such as partial least square. The authors highlighted that by knowing the characteristic of each product of a crude distillation unit, and follow a continuous probability distribution function; variables of the probability distribution function can be calculated from operating conditions in the same way. Two key ideas are used to identify the feed characteristic as a real time basis. The first is that the characteristic, TBP of component of feed and products, follows a specific probability function. The other is that the variables of the function can be correlated with operating conditions by using an inferential modelling technique such as partial least squares regression analysis.

Rigorous modelling such as PetroSim™ and Aspen HYSYS Crude™ are commercial software developed by KBC plc and Aspen Tech plc respectively for industrial used. PetroSim™ is a full-featured, graphical process simulator for rigorous modeling of refineries and petrochemical facilities. Aspen HYSYS Crude™ enables the simulation of crude oil assays and crude columns. It characterizes the hydrocarbon fluid by determining the hypothetical components that make up the oil and predicts their thermophysical and transport properties. Beside that, very sophisticated analytical

equipment likes NMR has also been used to indirectly predict the properties of petroleum fraction. Even though the rigorous modelling and NMR capable to predict very accurately the crude assay and its properties but they are too complex, lengthy and expensive (Hsu and Robinson, 2006).

2.4 Process optimisation

Overall refinery optimization is considered as one of the most difficult and challenging optimization tasks. Zhang et al. (2003) separate the issue into two parts, overall plant optimization and unit process optimization. The overall plant optimization focuses on plant-wide managerial issues, with not too much consideration of process details. Linear programming (LP) methods have been widely used for this application. However, LP methods are based on simplified correlations. It cannot describe the nonlinear and discrete reality accurately. This limits the application of LP methods to long-term planning with indicative results, but is not applicable for short-term scheduling and on-line optimization. For process unit optimization, it focuses on operating details. Rigorous models have been used to represent each process, which is much closer to the reality. Nonlinear programming (NLP) methods have been widely applied for optimization of individual processes. But the role played by each process towards the overall economics is not properly addressed and integrated with plant-wide optimization. The achieved accuracy of process optimization may be at the cost of the overall plant profit. A new approach is developed to make the overall problem mathematically solvable and computationally efficient, while integrating process optimization and capturing the non-linear and discrete nature of the problem. The authors proposed a novel decomposition strategy, which decomposes the overall problem into two levels, namely a site level and a process level optimization. In the site level, the objective is to maximize the overall plant profit by taking into account major aspects associated with plant-wide operation. With this decomposition, the site level optimization generates operating guidelines (e.g. feed conditions, allocation of utilities) for each process, while the process optimization generates updated yield performance for the site level optimization to re-evaluate feed conditions to each process.

Crude distillation unit (CDU) operations are often defined in several operating modes, which are still being used by quite a few refineries for their planning. However, these operational modes cannot reflect all the ever-changing operating conditions of a refinery. As a result, the CDU operation condition may be sub-optimal and potential profit may be lost. Wenkai Li et al. (2005) propose a CDU model to decide the weight transfer ratio (WTR) ranges of CDU fractions from the operation modes. These WTR ranges are integrated into the refinery planning model to obtain the optimal CDU operation condition. Another widely used method is swing cut modeling. Several swing cuts, physically non-existent, are defined in the LP model. The definition of swing cut is illustrated in Figure 2.3 below, where gross overhead (GO) and heavy naphtha (HN) are the two distillates of a CDU (Zhang et al., 2001).

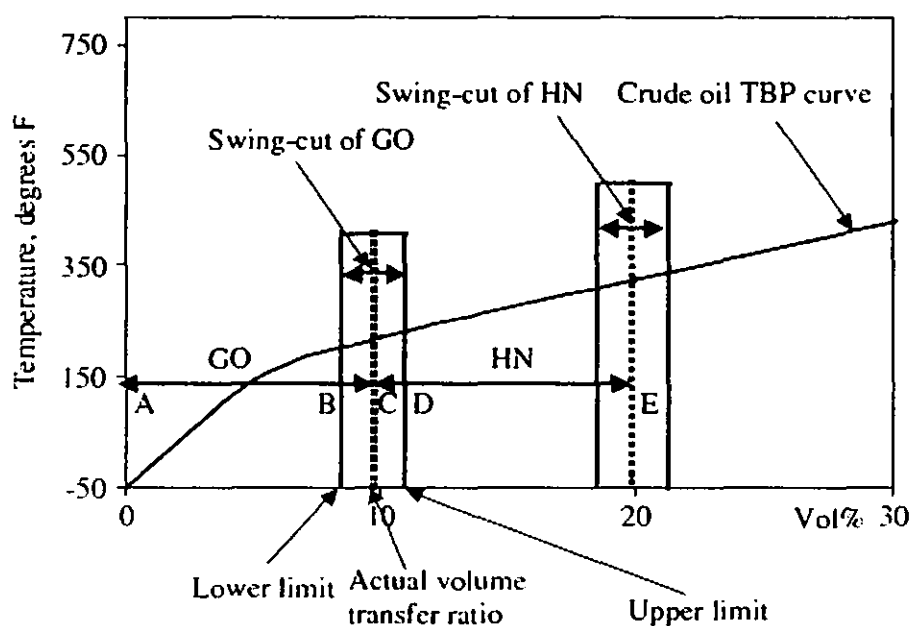


Figure 2.3: Swing cuts method (Zhang et al., 2001).

In general, two issues need to be considered in swing cut modeling: the sizes of swing cuts and the properties of the cut fractions. The size of a swing cut can either be expressed as certain VTR on crude feed or as a certain boiling temperature range. Zhang et al. (2001) used 5 and 7% VTR on crude feed as the sizes of naphtha and kerosene swing cuts respectively.

2.5 Summary

Crude oil characterisation & Technique to predict complete distillation data

Tareq A. Albahri, (2006)

- presented a novel technique predicting the thermo-physical and transport properties of light petroleum fractions using Molecularly Explicit Property Prediction Mode (MEPP) from ASTM D86 distillation data

Doug Hyung Lee et al, (2006)

- proposed a new approach predicting TBP curve using an inferential modelling technique e.g. partial least square

Riazi M.R (2005)

- developed characterisation of crude oil or C7+ fractions using 3 type distribution models to predict the complete distillation curve; namely exponential, gamma and generalised model

Wenkai et al.. (2005)

- proposed a simplified empirical nonlinear process models as alternative to unnecessary complications of rigorous process models imposes

Ramin et al., (2005)

- developed a set of conventional feed-forward multilayer neural networks to predict basic properties of pure compounds and petroleum fractions based on their normal boiling point (T_b) and liquid density at 293 K

Tirtha et al, (2004)

- proposed an algorithm that uses the crude TBP curve and other routinely measured variable e.g. flow rates, temperatures and pressures in CDU to predict the product properties.

Process optimisation

Juan Gomez-Prado et al (2008)

- optimised the refining process by integrating crude oil characterisation with refinery models to increase its “energy impact” through the production of more efficient and potentially cleaner fuels

Wenkai Li et al, (2007)

- proposed weight transfer ratio (WTR) ranges of CDU fractions from the operation modes to overcome CDU sub optimal operation and potential profit lost. These WTR ranges are integrated into the refinery planning model to obtain the optimal CDU operation condition.

Zhang et al (2003)

- Developed a new approach by separating the optimization process into two parts, overall plant optimization and unit process optimization

CHAPTER III

RESEARCH METHODOLOGY

3.1 Introduction

There have been significant achievements by researchers in development of mathematical modelling that enhance the conventional way of predicting feed distillation curves. From the literature review, two of the most significant methods were selected and used as base reference in this research study. These two are the General Distribution Method (GDM) and the Narrow Cut Method (NCM)

In this study, a hybrid modeling approach has been proposed for the following:

- (a) Simplifying feed synthesis method of reconstructing feed distillation curve from distillate product data
- (b) Predicting pure component distillation curve from the “reconstructed” blended feed distillation curve
- (c) Optimising the desired product yields at operating constraints

The main advantages of this proposed method is that, it does not require additional data apart from the one that are already available from routinely measured operating data such as feed and product flow rates, distillate product ASTM curve, pressure and temperature of both feed and product streams.

3.2 Spreadsheet modelling

In this research study, a spreadsheet modelling of the existing methods that used to predict feed distillation curves was developed in Microsoft Excel. The conversion of ASTM D2887 simulated distillation (SD) to TBP was carried out using AspenHYSIS™ software because the laboratory data available were beyond the

recommended range of typical empirical correlations method. The general steps required to develop the spreadsheet model is summarised in Figure 3.1 below.

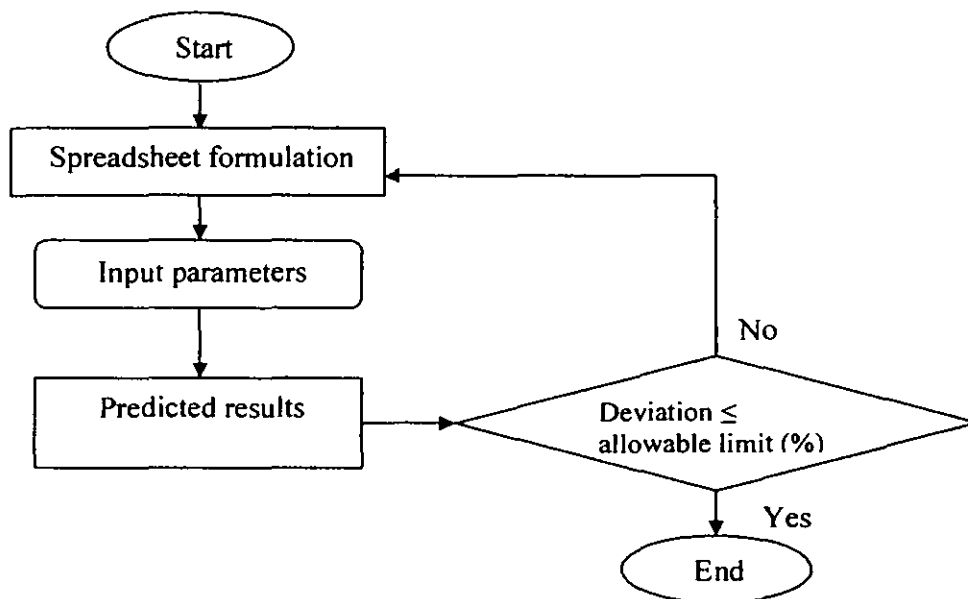


Figure 3.1 General process flow of spreadsheet modelling

The procedure is explained below:

Step 1: Spreadsheet formulation

The first step of spreadsheet modelling is to define the mathematical formulation of the existing and proposed methods. In this study, the non-linear equation of feed distillation curve; $y^n = mx^z + k$ is converted to linear equations, $y = mx + c$ using regression method and empirical correlations given by industry and / or published by researchers.

Step 2: Input parameters

The parameters to be used as an input to the above formulation are the actual laboratory results, such as normal boiling temperature (ASTM D86), SG, K_{vis} and etc.

Step 3: Results

The predicted results are examined by comparing against the actual laboratory analysis results. The deviation from actual data should not exceed the allowable limit.

If the result obtained is not meeting the requirement, repeat step (1) by checking the formulations.

Step 4: Acceptance criteria

The criterion for model validation is the deviation from actual data. The deviations are measure in many forms. In this study, the deviation are measured in term of absolute deviation (AD), average absolute deviation (AAD) and deviation co-efficient (R^2) of parity plot.

3.3 Prediction of basic feed distillation curves

The basic distillation curves of crude oil and condensate property are TBP, SG and K_{vis} . The existing methods to predict these distillation curves in blended condensates were studied and evaluated based on their accuracy, simplicity and compatibility. Among all the methods reported in the literatures, two methods were found suitable to be used in this study. They are the General Distribution Method (GDM) and the Narrow Cut Method (NCM).

3.3.1 General Distribution model

GDM is versatile and applicable to all major characterisation parameters with reasonable accuracy. It was reported that the method can predict a complete distillation curve, ranging from initial point (IP) to 95% point, as well as the properties from a limited available data. Once a distribution model is known, it can be split into a number of pseudo components (Riazi, 2007). However, the accuracy of this method is excellent for predicting TBP curve; it varies for bulk properties e.g. SG, K_{vis} and etc. A general equation used in GDM is given by equation 3.1 below.

$$\frac{P - P_o}{P_o} = \left[\frac{A}{B} \ln \left(\frac{1}{1 - x_c} \right) \right]^{1/B} \dots\dots\dots \text{equation 3.1}$$

where P is TBP or bulk properties and x_c is cumulative volume fraction

In equation 3.1 A , B and P_o are the three parameters to be determined from the available data through linear regression equation. For a linear equation in the form of $Y = C_1 + C_2 X$,

$$Y = \ln \left[\frac{P - P_o}{P_o} \right] \quad \dots\dots\dots \text{equation 3.2}$$

$$X = \ln \ln \left[\frac{1}{(1 - x_c)} \right] \quad \dots\dots\dots \text{equation 3.3}$$

$$B = \frac{1}{C_2} \quad \dots\dots\dots \text{equation 3.4}$$

$$A = B \exp(C_1 B) \quad \dots\dots\dots \text{equation 3.5}$$

GDM calculation procedures

The procedure for General Distribution model is made up of 5 steps as explained below:

Step 1: Guess P_o

Note that P is the properties of the feed where it can be either TBP or bulk properties e.g. SG, K_{vis} , RVP and etc. The initial guessed value P_o shall be \leq of its initial point, P_{IP} of that particular property at 0.5 cumulative yield (vol %).

Step 2: Develop linear regression

From the data given, calculate X and Y using equation 3.2 and equation 3.3 respectively. Note that equation 3.2 gives infinity answer at cumulative yield fraction $x_c = 1$. Since final boiling point (FBP) or End Point (EP) is a finite value, therefore $x_c = 0.995$ will be used as an approximate predicted value to represent the EP. For the bulk properties, the cumulative yield fraction, x_c shall be referred to average yield fraction which is defined as follows:

$$x_{c,i} = x_{c,i-1} + \frac{(x_{i-1} + x_i)}{2} \quad \dots\dots\dots \text{equation 3.6}$$

where x_i is volume fraction of i^{th} pseudo component, $i = 1, 2, 3, \dots n$

By using the calculated X and Y values, plots XY scatter type graph in Excel.

Step 3: Determine maximum coefficient R^2

From the line fitting or parity plot, the correlation coefficient R^2 is determined. By trial and error, the guessed property P_o that gives maximum R^2 is sought. The correlation coefficient R^2 is defined as:

$$R^2 = \frac{[N(\sum XY) - (\sum X) \times (\sum Y)]^2}{[N\sum X^2 - (\sum X)^2] \times [N\sum Y^2 - (\sum Y)^2]} \dots\dots\dots \text{equation 3.7}$$

where N is the number of data points.

Step 4: Determine gradient m and constant c at maximum R^2

At P_o that gives maximum R^2 , the gradient m and constant c of the straight line fit is determined. Equation 3.4 and equation 3.5 are used to calculate the parameter A and B .

Step 5: Calculate predicted P

Finally, calculate predicted P at cumulative yield fraction, x_c using equation 3.1

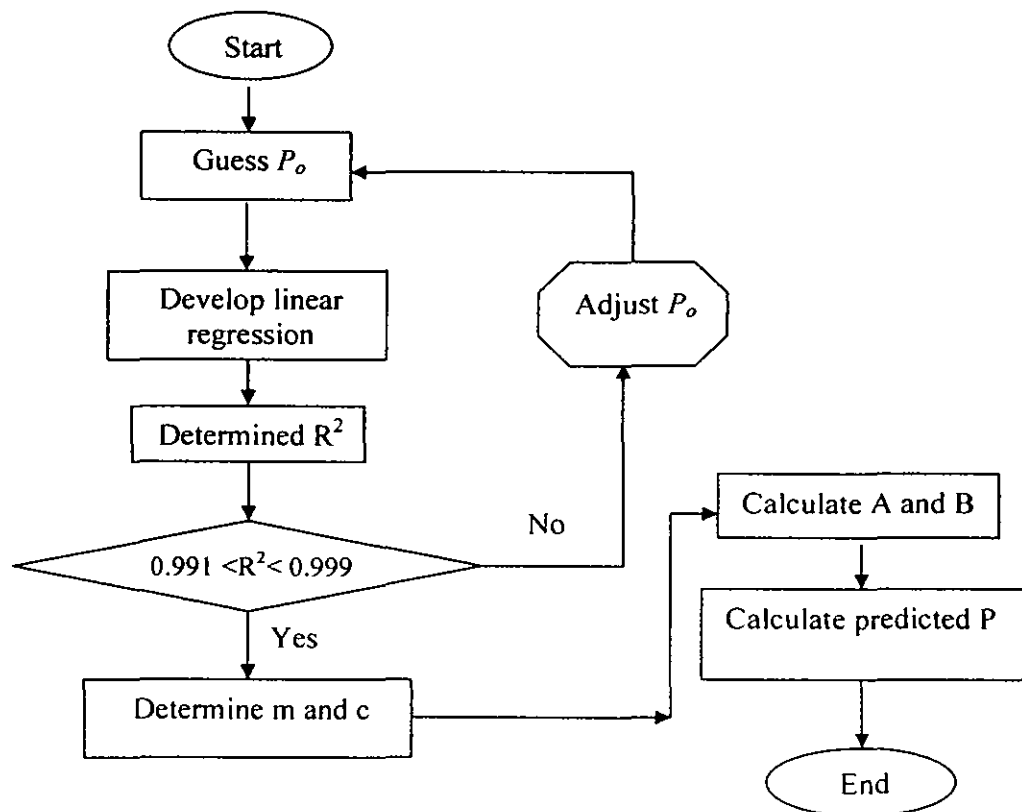


Figure 3.2 Algorithm for General Distribution method

The algorithm of GDM to predict TBP curve and properties distribution in condensates is given in Figure 3.2.

3.3.2 Narrow Cuts Model

The model was derived from a conventional method called “Narrow Cut Method”, NCM. The method has widely been used to predict bulk properties distribution in crude oils (Parkash, 2003). Basically the wide cuts fractions such as Light Straight Run Naphtha (LSR), Heavy Straight Run Naphtha (HSR) and kerosene from blended condensates are divided and split into smaller cuts. These cuts are referred to as pseudo-components. The properties of pseudo-components are calculated and corrected iteratively until the predicted values of wide cuts converge with the starting input value. The algorithm of NCM to predict TBP curve and properties distribution in condensates is given in Figure 3.3.

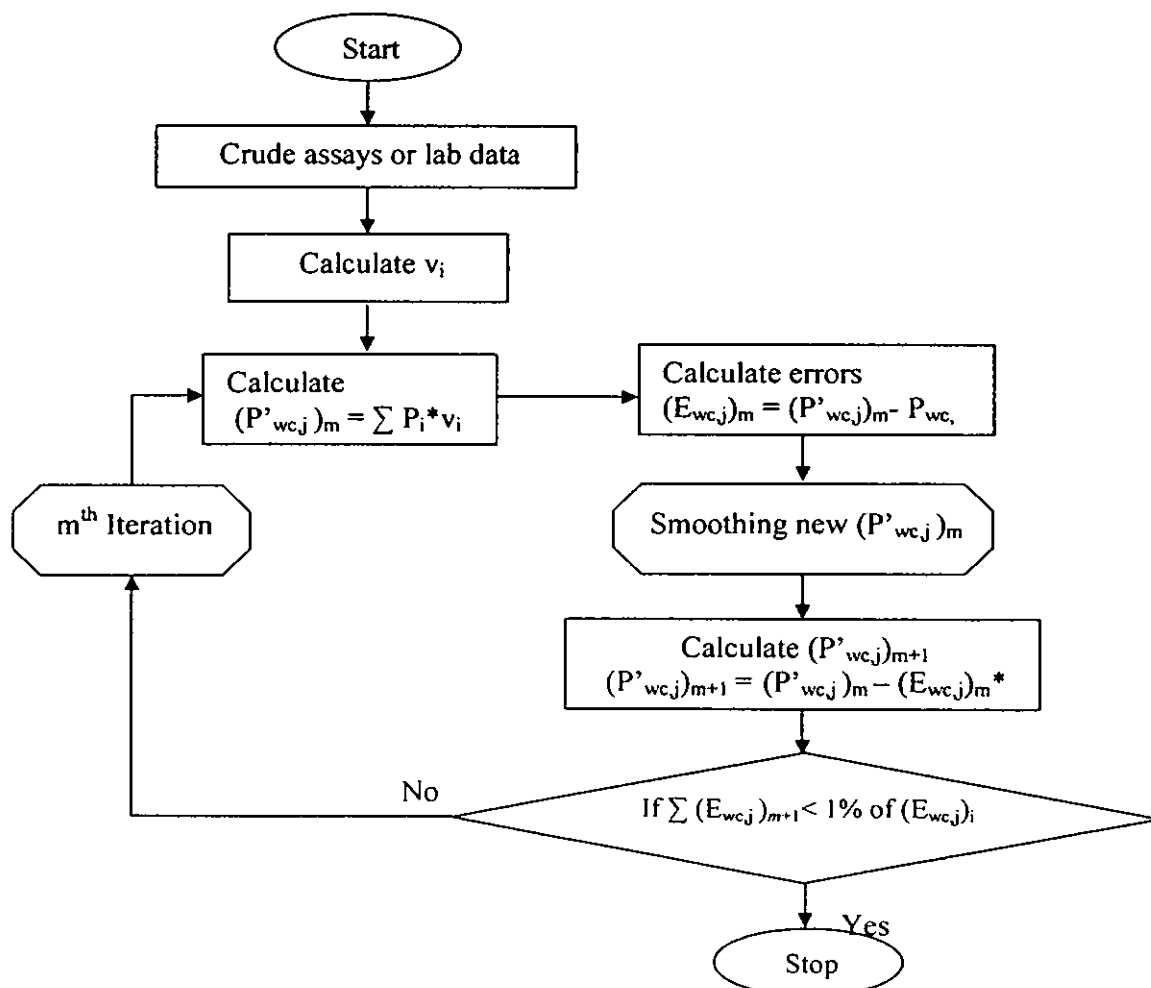


Figure 3.3 Algorithm for Narrow Cut method

NCM calculation procedures

Step 1: Divide the wide cuts into narrow cuts of pseudo components

All the wide cuts of the blended condensates are divided into pseudo-components each with 5°C boiling range. The volume fraction of each pseudo-component, v_i is calculated using equation 3.9 below.

$$v_i = \frac{v_{wc,j}}{\sum v_{cw,j}} \dots\dots\dots \text{equation 3.9}$$

where $v_{wc,j}$ is volume fraction of the j^{th} wide cut

Step 2: Calculate $P'_{wc,i}$

Once v_i for all pseudo components are known, the predicted property of the wide cut, $(P'_{wc,j})_m$ may be determined from equation 3.10:

$$(P'_{wc,j})_m = \sum P_i * v_i \dots\dots\dots \text{equation 3.10}$$

where m is the number of iterations.

Starting at $m = 0$, let assumed the predicted property for each cuts are the same as such $(P'_{wc,j})_0 = (P'_{wc,j+1})_0 = (P'_{wc,j+2})_0 = (P'_{wc,n})_0$, hence

$$(P'_{wc,j})_0 = \frac{(P_{wc,j+1} + P_{wc,j+2} + \dots\dots P_{wc,n})}{N} \dots\dots\dots \text{equation 3.11}$$

where N is total number of fractions in blended condensates.

Step 3: Check errors, $E_{wc,j}$

The error, $(E_{wc,j})_m$ is defined as $(P'_{wc,j})_m - P_{wc}$, is calculated as the difference between the predicted and the actual properties.

$$(E_{wc,j})_m = \frac{|(P'_{wc,j}) - (P_{wc,j})|}{P_{wc,j}} \times 100\% \dots\dots\dots \text{equation 3.12}$$

where $P'_{wc,j}$ is calculated property and $P_{wc,j}$ is input property

Step 4: Calculate a new $(P'_{wc,i})_{m+1}$

A new property of wide cut is calculated by using equation 3.11:

$$(P'_{wc,i})_{m+1} = (P'_{wc,i})_i - E_{wc,j} * V_i / \sum V_i \dots\dots\dots \text{equation 3.13}$$

Step 5: Recalculate $P'_{wc,i}$

Note that after first iteration, many of the adjacent pseudo-components still have identical values and there are sharp discontinuities where wide cut boundary occur. Therefore prior to recalculating the predicted property, it is first needed to smooth out this sharp discontinuity of the wide cuts. The smoothing procedure is briefly described as follows:

Smoothing procedure

For most cuts, four components are required to determine a new smoothed property for each pseudo-component (Parkash, 2003). The procedure is illustrated in Figure 3.4:

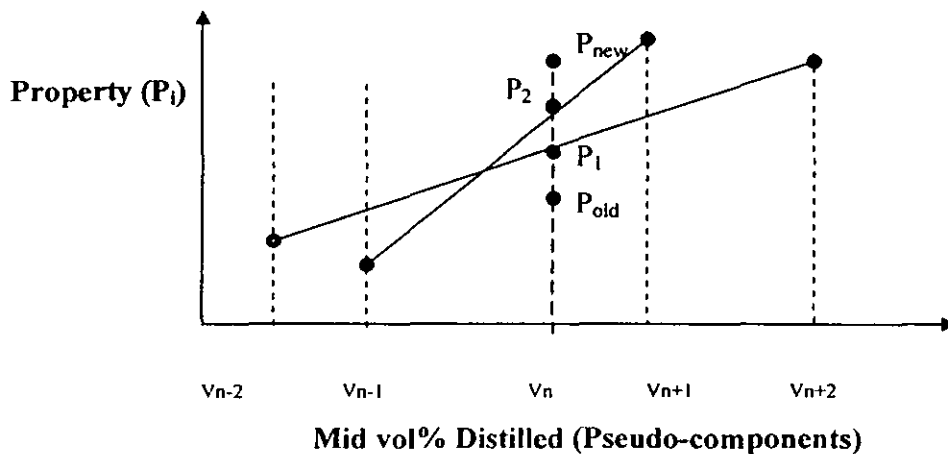


Figure 3.4 Smoothing procedure

Where P_{old} = value of property nth cut (unsmoothed value), P_1 =linear interpolation between V_{n-2} and V_{n+2} , P_2 =linear interpolation between V_{n-1} and V_{n+1} , P_{new} = value of property nth cut (smoothed value) and $P_{new} = 0.4x P_{old} + 0.4 x P_2 + 0.2 x P_1$
 An example of smoothing procedure (Parkash, 2003) is given in Table 3.1:

Table 3.1 Example of smoothing procedure after the first iteration

Pseudo-component	1 st iteration	Smoothed value
n	a	a
n + 1	b	$0.5 \times b + 0.5 \times (a + b)/2$
n+ 2	c	$0.4 \times c + 0.4 \times (b + d)/2 + 0.2 \times (a + e)/2$
n+ 3	d	$0.4 \times d + 0.4 \times (c + e)/2 + 0.2 \times (b + f)/2$
n+ 4	e	$0.5 \times e + 0.5 \times (d + f)/2$
n+ 5	f	f

Step 6: Check convergence criteria

Convergence is achieved by repeating Step 3 to step 5 until $\sum(E_{wc,j})_{m+1} < 0.01 * (E_{wc,j})_m$

3.4 Predicting distillation curves in blended condensates

The models of the existing methods described in section 3.4.1 and 3.4.2 above were used to predict TBP curve and properties distribution in the blended feedstock.

3.4.1 Condensates used in the study

In this study, two pure Malaysian condensates namely; Bintulu Condensate (BNC) and Terengganu Condensate (TNC) were used in the spreadsheet modelling. The original laboratory analysis (condensate assays) of these pure condensates is given in Appendix 3.1.

3.4.2 TBP and bulk properties data

The data for TBP and bulk properties of the blended condensates are taken either from lab analysis or original crude assay.

TBP data

The feed to CFU is analysed in laboratory using Simulated Distillation (SIMDIST) method. Simulated Distillation (SD) is a simple method that gives good accuracy. It takes about three hours to perform the analysis which include sampling, preparation of the samples and two chromatographic runs (Falla et al., 2005). The conversion from SD to TBP can be done using Daubert's method. The details are given in Appendix 1. However, the boiling temperature range of the blended feed used in this study exceeding the allowable limit specified by Daubert's method, thus the conversion is carried using process simulation software; PetroSIM™, the KBC SIM modelling software.

Bulk properties data

Laboratory analysis of the bulk properties requires standard procedures defined by ASTM and API. In this study, the bulk properties of the blended condensates were estimated from original laboratory results in the form of condensate assays. Using standard mixing rules given by equation 3.12 (Parkash, 2003), the bulk properties are estimated from the properties of individual cuts or fractions.

$$P_i = \sum_{j=1}^n p_{i,j} \times x_{i,j} \quad \dots\dots\dots \text{equation 3.12}$$

In equation 3.12, P is a bulk property of blended condensates and p is bulk property of pure condensate. The subscript i is i^{th} pseudo-component where the subscript j is crude type; $j=1, 2, 3, \dots, n$.

The crude assay usually provides information on limited number of cuts. Normally only SG is given. Therefore the desired information of other bulk properties on specific cuts is normally obtained by approximation (Parkash, 2003). In this study, the unknown properties are calculated using mass balance as given in equation 3.13.

$$P'_k = \frac{(P'_{\text{overall}} \times \sum P'_i x_i)}{x_k} \quad \dots\dots\dots \text{equation 3.13}$$

where P' is bulk properties blending index of the whole mixture and P'_k estimated bulk property for k^{th} cut point

For the non linear additive properties like kinematic viscosity, K_{vis} it shall be converted first to its blending index K'_{vis} as given by equation 3.14 below.

$$K'_{vis} = 23.097 + 33.468 \log(\log(K_{vis} + 0.8)) \dots \dots \dots \text{equation 3.14}$$

Even if more than two data for a particular bulk property at specific cuts is not given, the bulk property for these cuts still can be determined by trial and error. However, for simplicity, equation 3.13 is only used for bulk properties where only one fraction is not given, otherwise they were ignored. The algorithm to acquire TBP and bulk properties data for blended condensates is given in figure 3.5 below.

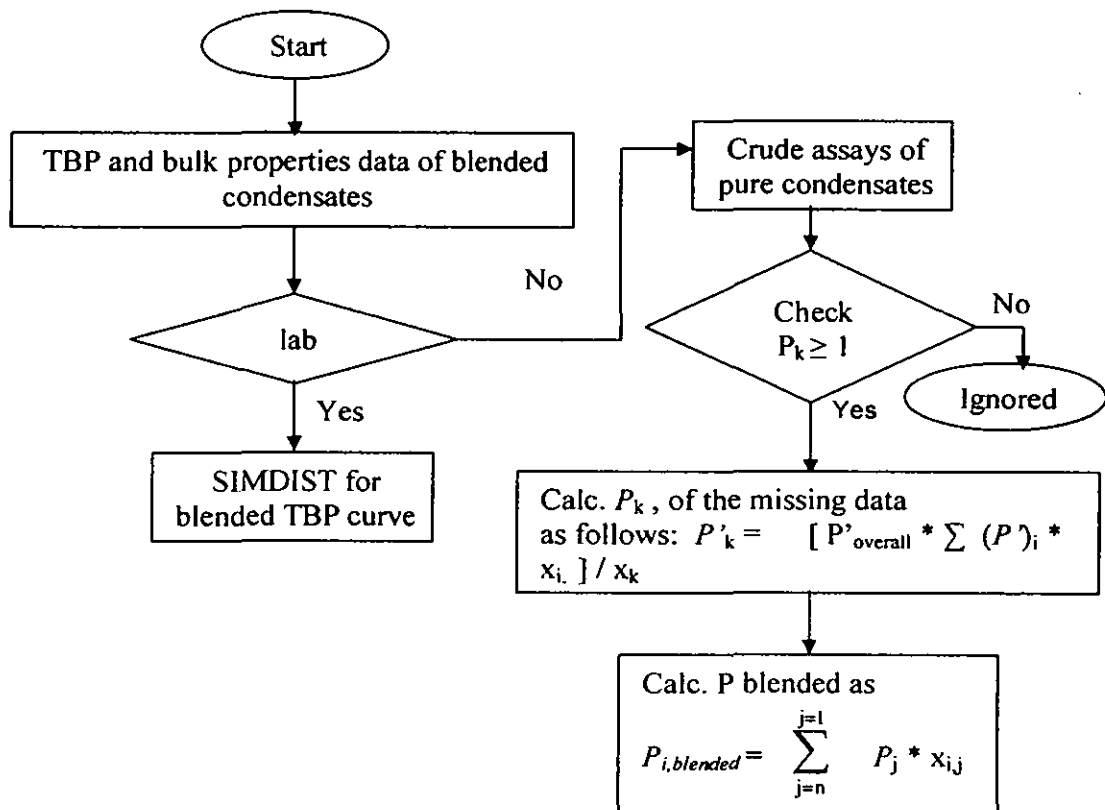


Figure 3.5 Algorithm to acquire data for blended condensates

3.4.3 Model Validation

The models are validated by comparing the deviation of predicted values against the experimental data. In this study, the percentage of absolute average deviation

(%AAD), parity plot and error squared of the overall mixture E_p^2 were used for model validation. %AAD is basically used to measure the average deviation of the predicted results against the experimental data (Riazi, 2005) as per equation 3.15 below.

$$\%AAD = \frac{1}{n} \times \sum_{i=1}^{i=n} |\%D| \quad \dots\dots\dots \text{equation 3.15}$$

where $|\%D|$ is percent relative deviation, $\%D_i = \frac{(P'_i - P_i)}{P_i} \times 100\%$.

P_i and P'_i is an experimental value and predicted value for i^{th} pseudo-component respectively, and n is the total number of input data

In addition, E_p^2 is used to calculate the error of the bulk properties for the whole range pseudo-components against experimental data. Equation 3.16 shows the calculation of E_p^2 .

$$E_{P,mix}^2 = \frac{|(P'_{mix} - P_{mix})|}{P_{mix}} \times 100\% \quad \dots\dots\dots \text{equation 3.16}$$

where P and P' is an experimental value and predicted value respectively for the whole range of the mixture.

A parity plot is also used to validate the model. The graph of predicted results and experimental values is plotted. From the graph, correlation coefficient R^2 of the fitting line is determined. R^2 reflects the accuracy of the model. The closer the value of R^2 to 1, shows better accuracy.

3.5 A proposed method to predict feed TBP curve and SG distribution in pure condensate

The existing methods discussed in previous sections are applicable to predict TBP and bulk property distribution in pure condensate feed. However, these methods are not suitable to predict directly TBP and bulk property distributions in a mixture of different condensates or “blended Feed”.

To overcome the deficiency of the current approach, a new method of “Pseudo-component Linear Equation” (PcLE) is proposed. PcLE is capable of predicting

individual component (pure condensate) TBP and SG distillation curve from blended feed. The basic principle of this method is to decompose the nonlinear TBP and SG curves of the blended condensates into a series of linear pseudo-components curve. The combination of GDM to model the blended feed distillation curve with PcLE method would create a short cut to predict TBP curve and SG distribution of each individual component in the blended feed without having to perform laboratory analysis on individual feed sample.

3.5.1 The concepts of PcLE method

In most cases, TBP curve and bulk properties distribution in condensate are non-linear. This non-linear curve is basically made up from a series “pseudo components” curve. Figure 3.6 below illustrated the non-linearity of TBP curve. If this non linear curve is decomposed into several cuts or pseudo components as denote as Pc-0, Pc-1 and Pc-3, it gives almost a linear TBP curve for each pseudo component. Note that, the smaller the cut range; the linear will be the curves.

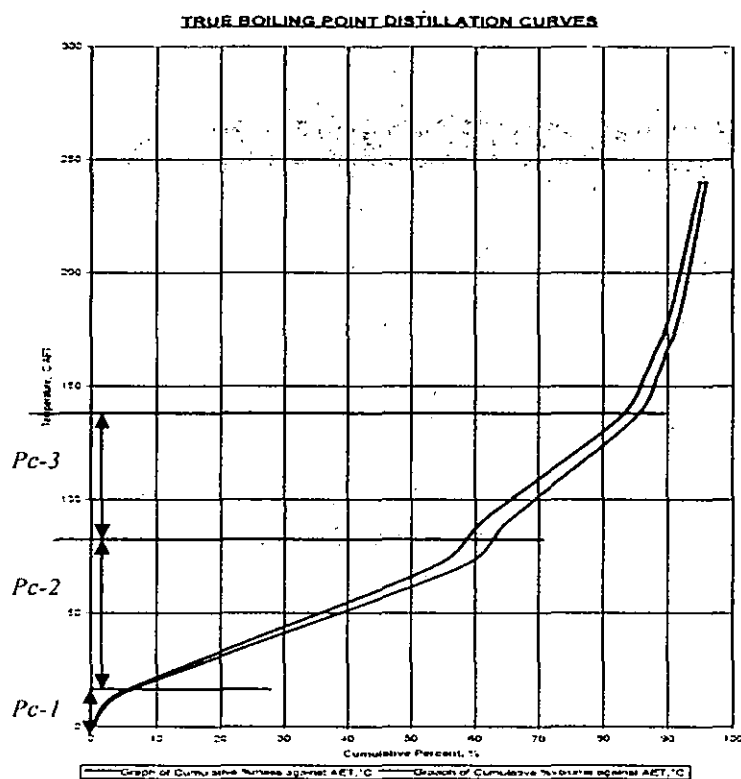


Figure 3.6 A typical non linear TBP curve

Therefore, by breaking up this non-linear curve into smaller cut points has enabled development of a series of pseudo component linear equations (PCLEs) as illustrated in figure 3.7.

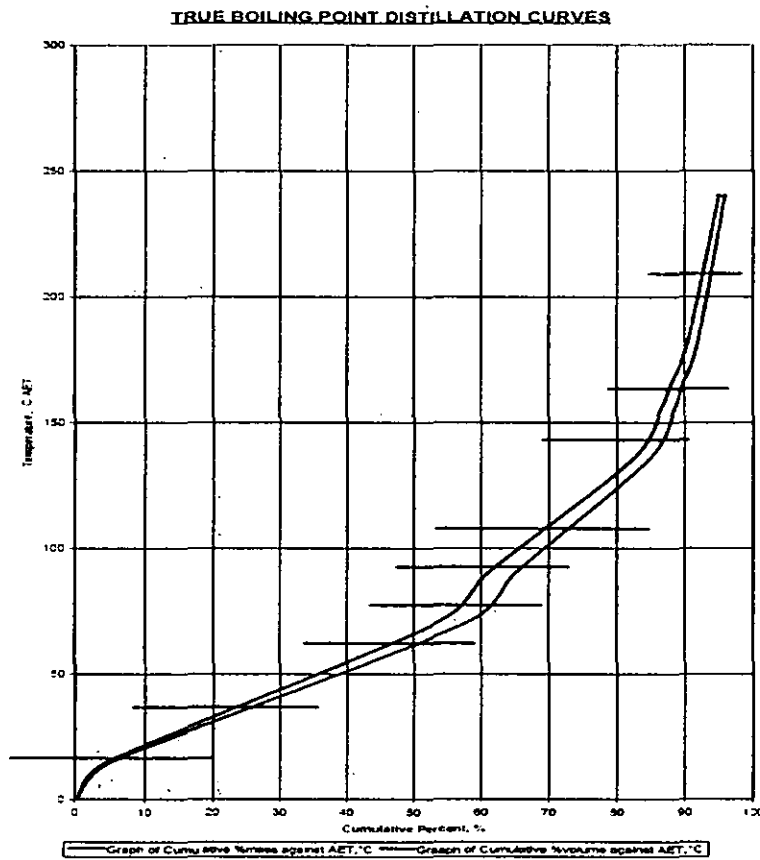


Figure 3.7 A series of pseudo component linear curves in non linear TBP curve

For any two pseudo-components from pure condensates, a composite of the two linear equations can be developed. The first pseudo component has a yield fraction of 15 vol% within a boiling range -5 °C to 15 °C. Additionally, the second pseudo component has a yield of 8 vol% within boiling range of 15 °C to 70 °C. The linear equations of these pseudo-components are given by equation 3.17 and 3.18 below:

$$y_i = m_i x + c_i \quad ; \quad y_i (x) \leq 15 \text{ }^\circ\text{C} \quad \dots\dots\dots\text{equation 3.17}$$

$$y_{i+1} = m_{i+1} x + c_{i+1} \quad ; \quad y_{i+1} (x) \leq 70 \text{ }^\circ\text{C} \quad \dots\dots\dots\text{equation 3.18}$$

where y is TBP, x is cumulative volume fraction (%), and i is the ith number of pseudo-component with specific boiling range.

TBP is a function of cumulative volume fraction with a specific upper limit. Beyond the upper limit, the linear equation of $(i+1)^{\text{th}}$ pseudo component will be used. This approach avoids “overshooting” by the trajectory of i^{th} pseudo component linear equation. Therefore the cumulative volume fraction, x_c at any TBP can be determined as such:

If $-5\text{ }^{\circ}\text{C} < \text{TBP} < 15\text{ }^{\circ}\text{C}$, y_i is used,

Else if $15\text{ }^{\circ}\text{C} < \text{TBP} < 70\text{ }^{\circ}\text{C}$, then y_{i+1} is used

Figure 3.8 illustrates the adjacent pseudo-components are link together.

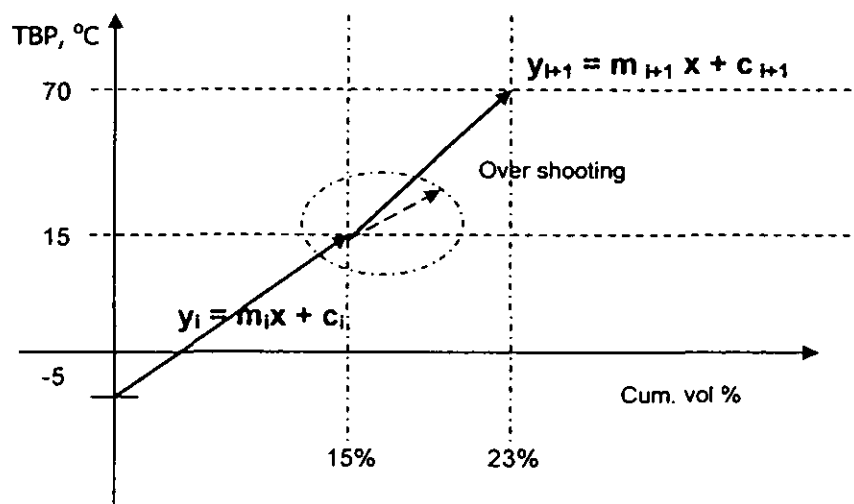


Figure 3.8 Two adjacent linear equations are link using PcLE method

This method gives good accuracy of estimating TBP-curve and bulk properties distribution because x_c of pseudo-component is calculated within the boundary of the defined boiling range.

During condensate blending, no chemical reaction is assumed to take place. Thus when two or more condensates are mixed together, the linear equation of the mixture is the summation of linear equation of each pseudo-component of the same boiling range in the mixture multiplied by its respective blending ratio as given in equation 3.19.

$$y_{i,j\dots n} = \sum_{j=1}^n \alpha_j \times (mx + c_i) \dots\dots\dots \text{equation 3.19}$$

where $i = i^{\text{th}}$ pseudo-component

j is crude type; $j=1,2,3,\dots,n$, and

$$\alpha \text{ is blending ratio in \% is calculated as } \alpha_j = \frac{V_j}{\sum V_j} \times 100\%$$

For any two pure condensate A and condensate B, the linear equation for the pseudo-component within the same boiling range can be expressed as:

$$y_{A,i} = m_{A,i}x + C_{A,i} \dots\dots\dots \text{equation 3.20}$$

$$y_{B,i} = m_{B,i}x + C_{B,i} \dots\dots\dots \text{equation 3.21}$$

where equation 3.20 and 3.21 is the linear equation of pure condensate A and condensate B respectively.

For blended condensate, equation 3.20 and 3.21 form a composite line expressed as follows:

$$y_{AB,i} = m_{AB,i}x + C_{AB,i} \dots\dots\dots \text{equation 3.22}$$

where

$$m_{AB,i} = \alpha_A * m_{A,i}x + \alpha_B * m_{B,i}x$$

$$C_{AB,i} = \alpha_A * C_{A,i} + \alpha_B * C_{B,i} \text{ and}$$

$$\alpha_A + \alpha_B = 1 \dots\dots\dots \text{equation 3.23}$$

Substituting $\alpha_B = 1 - \alpha_A$ into equation 3.22

$$y_{AB,i} = \alpha_A * (m_{A,i}x + C_{A,i}) + (1 - \alpha_A) * (m_{B,i}x + C_{B,i}) \dots\dots \text{equation 3.24}$$

For a fixed interval i , as m changes, the slope of resulting line changes as well. The resulting yield (cumulative vol %) $x_{A,i} < x_{AB,i} < x_{B,i}$. The details are illustrated in Figure 3.9.

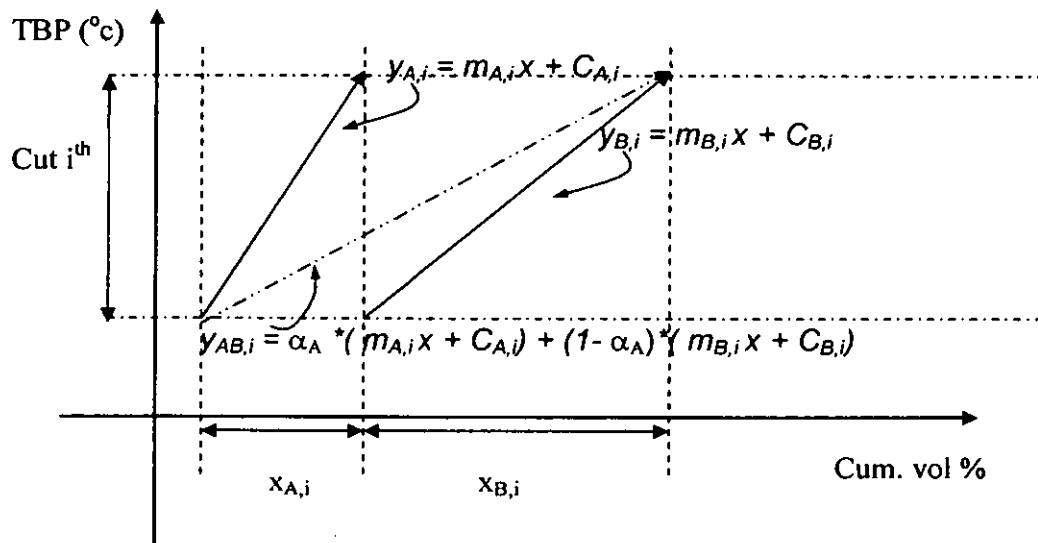


Figure 3.9 Composite linear equation of blended condensates for i^{th} pseudo-component

Use PcLE method to predict pure condensate distillation curves from blended feed

The PcLE method is capable of estimating single linear equation from composite of linear equations. The simplicity of the method enables it to predict pure component TBP-curve and bulk property distribution from blended feedstock if the blending ratio α in the mixture is known. The algorithm of PcLE method to predict pure condensate TBP-curve from blended feed is given in Figure 3.10

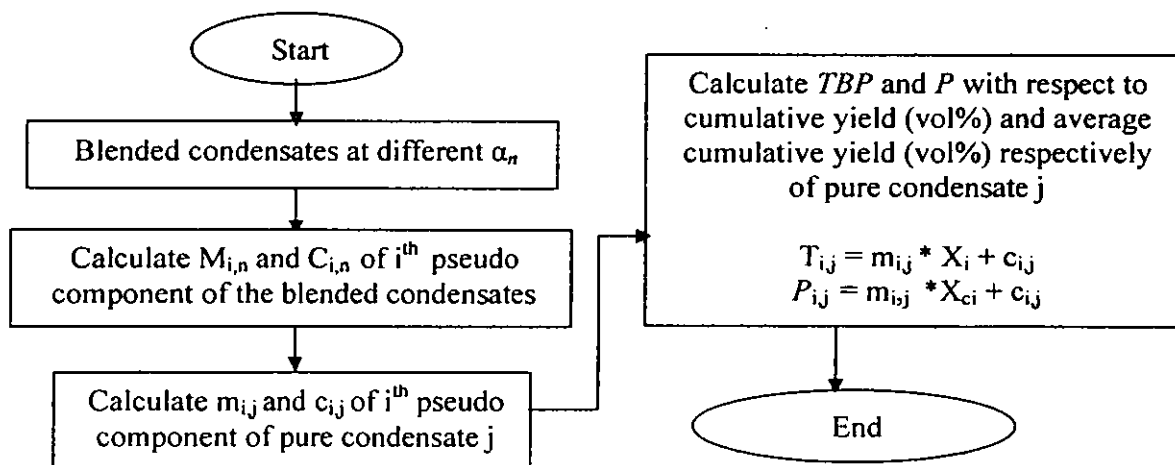


Figure 3.10 Algorithm of PcLE method predicting TBP and P from blended condensate

Brief description using PcLE method to predict pure condensate TBP from blended feed is explained as the following.

Step 1

Firstly, the linear equation of i^{th} pseudo component of the blended condensates at different α is determined.

Step 2

For n numbers of pure condensate j in the mixture, n sets of i^{th} pseudo component linear equation is determined, each at different α . Calculate the gradient, $M_{i,n}$ and constant, $C_{i,n}$.

Step 3

Calculate m_{ij} and c_{ij} of i^{th} pseudo component of pure condensate j using Gauss Elimination method.

Step 4

Finally, the TBP curve and P distribution for the whole range of pure condensate j is developed using equation 3.24 and 3.25 below.

$$T_{ij} = m_{ij} * X_i + c_{ij} \quad \dots\dots\dots \text{equation 3.24}$$

$$P_{ij} = m_{ij} * X_{ci} + c_{ij} \quad \dots\dots\dots \text{equation 3.25}$$

3.6 A proposed GDM-PcLE method to predict individual component TBP & SG curves

As mentioned in the previous section, TBP and SG have been widely used to determine other bulk properties in pure and blended feed. Therefore they are the important parameters for feedstock characterisation. Most of the laboratory analysis and characterization tests are time consuming. As being practices nowadays, only one parameter will be done and used to calculate the other curves using empirical regression functions (Riazi, 2005). Equation 3.26 shows the empirical regression function to convert the desired function from available data.

$$T_i(\text{desired}) = a[T_i(\text{available})]^b SG^c \dots\dots\dots \text{equation 3.26}$$

Where;

- i) $T_i(\text{available})$ and $T_i(\text{desired})$ is the available distillation temperature and the desired temperature at a specific vol% distilled, both are in Kelvin
- ii) SG is specific gravity of fraction at 15.5 °C
- iii) a, b and c are correlation parameters, specific for each conversion type and cumulative yield (vol%) of the distillation curve

Dutt (1990) found a simple method to calculate viscosity. The method needs only the average boiling point that referred to 50% boiling point (TBP_50(wt%)) as the only input. The method has been used to predict the viscosities of petroleum crude oils and their fractions with comparable or better accuracy than other methods, when tested on 15 world crude oils (and their fractions) at 250 data points, yielded an overall deviation of 6%.

$$\ln \nu = -3.0171 + \frac{442.78 + 1.6452 \times t_b}{t + (239 - 0.19t_b)} \dots\dots\dots \text{equation 3.27}$$

where ν is viscosity, t is reference temperature e.g. 30°C or 99°C and t_b is average boiling point. $K_{vis} = \nu / SG$

The vapour pressure of petroleum fractions can be calculated using average boiling point by correlation of Van Kramen and Van Ness (Parkash, 2003) as shown in equation 3.28 below.

$$P_{vap} = 0.0193210^x \dots\dots\dots \text{equation 3.28}$$

$$P_{vap} \text{ is vapour pressure in psi where } x = 6.07918 - 3.19837 \frac{(232 + B)}{232 + T} \left[\frac{(1120 - T)}{1120 - B} \right]$$

B is average boiling point (°C) and T is reference temperature (°C). RVP is the absolute pressure exerted by a mixture at temperature 37.8 °C, thus RVP is calculated using Equation 3.28 at $T = 37.8$ °C.

Goosen (1996) proposed a simple indirect method that capable to predict the molecular weight (MW) of petroleum fraction for C5 to C120. The method requires the TBP_50(wt%) and density only. It is demonstrated that the 50 wt % TBP of

fractions is equivalent to the normal boiling point of pure compounds. The new method has been compared to the API procedure 2B2.1 (1987), excellent results are obtained with a standard deviation of about 2%, which is at least 3 times better than that of published methods. The most common approach to predict blended feed TBP curve and SG distribution are by synthesis them using distillate products data (Tirtha, 2003).

In this study, the current method is further enhanced by adopting hybrid GDM-PcLE method to predict pure condensate TBP curve and SG distribution in pure condensate from blended Feed. The proposed procedure could assist plant engineers to characterise each of pure condensates used in the blending Feed. The information can be further used to explore and exploit the flexibility of the column operating parameters. The ultimate aim is to optimise the desired product yields. Figure 3.11 below described the hybrid GDM-PcLE method.

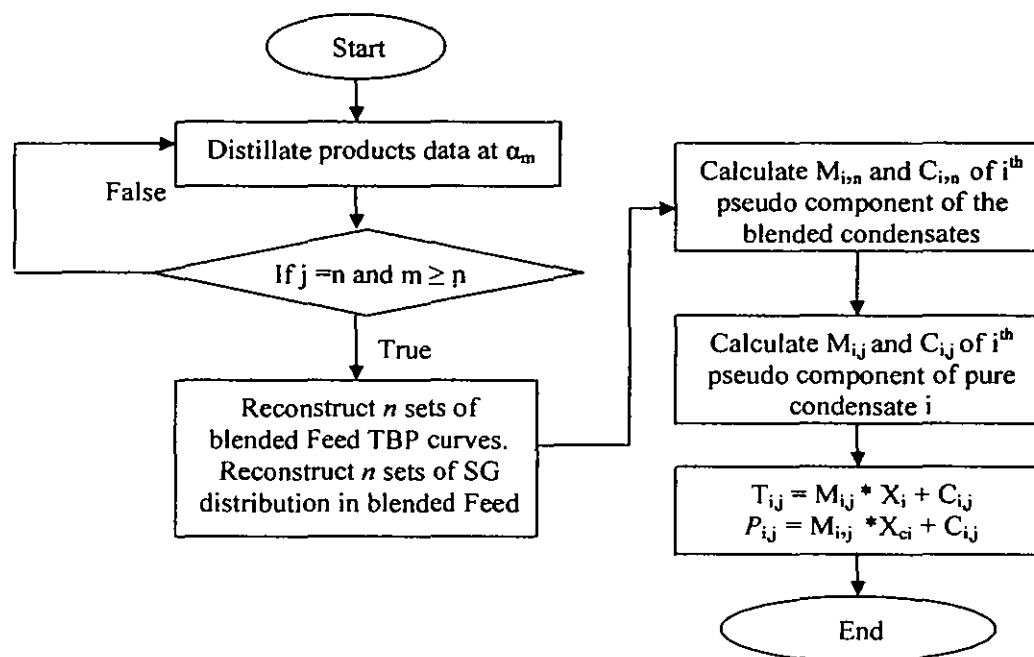


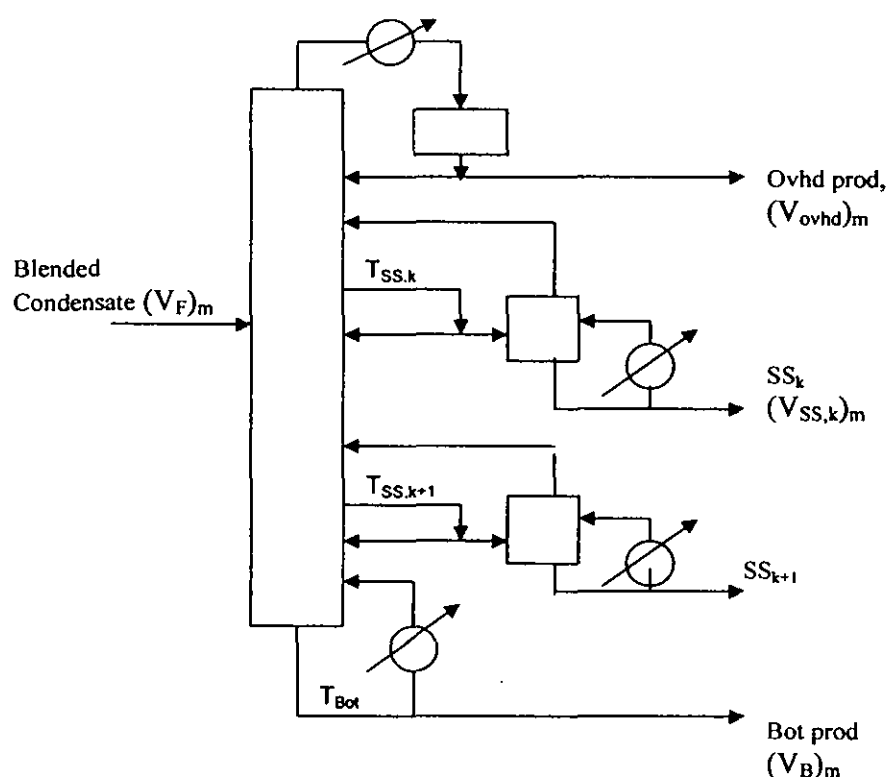
Figure 3.11 Algorithm for hybrid GDM-PcLE method to predict pure condensate TBP and SG distribution in pure condensate

Step 1: Distillate products data

In this step, blended feed flow rate and lab analyses on the distillate products at specific blending ratio, α , are required. The column feed stream is blended condensate

and produces three product streams at overhead, side stream and bottom of the column. A schematic diagram of distillation column is given in Figure 3.12.

The required column operating parameters are the feed and distillate products flow rates. Additionally the distillate product parameters required are the ASTM distillation and specific gravity.



*Note: m is number of data at different feed blending ratio, α_m
 $k = 1, 2, 3, \dots, z$ refers to number of side stream products*

Figure 3.12 Schematic diagram of Condensate Distillation Column

Empirical methods for converting various distillation data has began in the late 1920s and continued through 1950-60 by a large number of researchers where the results were adopted in the API-TDB (Riazi, 2005). Since TBP is more prominent compare to ASTM and SD, several methods from API Technical data book were used for inter-conversion (Riazi, 2005) as shown below. The details are given in Appendix 2.

Conversion ASTM 86 to TBP using Riazi-Daubert method

$$TBP = a \times (ASTMD86)^b \quad \dots\dots\dots\text{equation 3.29}$$

Conversion TBP to Equilibrium Flash Vaporisation (EFV) using Daubert method

$$EFV = a \times (TBP + 273)^b \times (SG)^c - 273 \quad \dots\dots\dots\text{equation 3.30}$$

where a , b and c are empirical correlations.

Conversion SD to TBP (Daubert's method)

$$V_i = C \times W_i^{D^b} \quad \dots\dots\dots\text{equation 3.31}$$

where V_i = difference in TBP between two cut points (K or °C)

W_i = Observed difference in SD temperature between two cut points (K or °C)

C and D are constants varying for each cut points

Step 2: Adequacy of data available

The blending ratio α_m refers to m^{th} feed blending ratio and j is the type of condensate used in blended feed where $j = 1, 2, 3 \dots n$. Therefore the procedure requires n sets of data comprising distillate product ASTM distillation and SG at different feed blending ratio, α_m . Hence $m \geq n$

Step 3: Reconstruction blended feed TBP curve

In this step, data from distillate products in step 1 will be used to reconstruct the feed TBP curve and SG distribution in blended feed.

Procedure to Reconstruct Feed TBP curve:Step 3.1: Convert ASTM distillation to TBP

The lab results for all distillate products are given in ASTM distillation. Daubert's method was selected for the conversion of ASTM distillation to TBP curve. This is due to method covering a wider range of cut points (IP, 10%, 30%, 50%, 70%, 90% and EP). The detail of Daubert's method is given in Appendix 3.

Step 3.2: Calculate the cumulative volume percentage of the blended feed

The blended feed, X_{Feed} at various fractions of Distillate products is X_{Feed} is defined as per equation 3.21 below.

$$X_{Feed,x} = \frac{x_{Distillate,i} \times (1 + X_{Distillate,i-1})}{\sum_{i=n} x_{Distillate,i}} \quad \dots\dots\dots \text{equation 3.32}$$

Where

x is cumulative vol.% of Distillate products

i^{th} is the distillate product where $i = 1, 2, 3 \dots\dots n$

A blended condensate is basically composed of all distillate products that are separated from the distillation column. However, distillation is not perfect where the distillate products may contain lighter and heavier component that boils below and above the product cuts respectively (Parkash, 2003). Generally <20% and > 80% of the distillate product is discounted for these lighter and heavier components. The TBP within these upper and lower ranges shall not be used to reconstruct Feed TBP curve. In this study, the TBP (X_{Feed}) is assumed equivalent to TBP ($x_{D,i}$) at the following fractions of Distillate products:

- (a) 10% of top product
- (b) 50% of all distillate products including top and bottom products
- (c) All distillate product's cut points
- (d) 90% of bottom product

The volume fractions of distillate products equivalent to TBP feed are summarised in Table 3.2.

Table 3.2 the fraction of distillate product equivalent to feed TBP

	TBP of Distillate Products	TBP of Blended Feed Equivalent
T1	$TBP_{10, \text{ovhd prod}}$	TBP_{IP}
T2	$TBP_{50, \text{ovhd prod}}$	$TBP_{(50\% \text{ of Ovhd prod} / \text{total prod})}$
T3	$(TBP_{EP, \text{ovhd prod}} + TBP_{IP, SS, i}) * 0.5$	$TBP_{(\text{Ovhd prod} / \text{total prod})}$
T4	$TBP_{50, SS, i}$	$TBP_{(\text{Ovhd prod} + 50\% SS, i / \text{total prod})}$
T5	$(TBP_{EP, SS, i} + TBP_{IP, SS, i+1}) * 0.5$	$TBP_{(\text{Ovhd prod} + SS, i / \text{total prod})}$
T6	$TBP_{50, SS, i+1}$	$TBP_{(\text{Ovhd prod} - SS, i + 50\% SS, i+1 / \text{total prod})}$
T7	$(TBP_{EP, SS, i} + TBP_{IP, Bot. prod}) * 0.5$	$TBP_{(\text{Ovhd prod} - SS, i + SS, i+1 / \text{total prod})}$
T8	$TBP_{50, \text{Bottom product}}$	$TBP_{(\text{Ovhd prod} - SS, i + SS, i+1 + 50\% Bot prod / \text{total})}$
T9	$TBP_{90, \text{Bottom product}}$	$TBP_{(\text{Ovhd prod} - SS, i + SS, i+1 + 90\% Bot prod / \text{total})}$

Figure 3.13 below illustrated the reconstruction of blended feed TBP curve from Distillate products TBP.

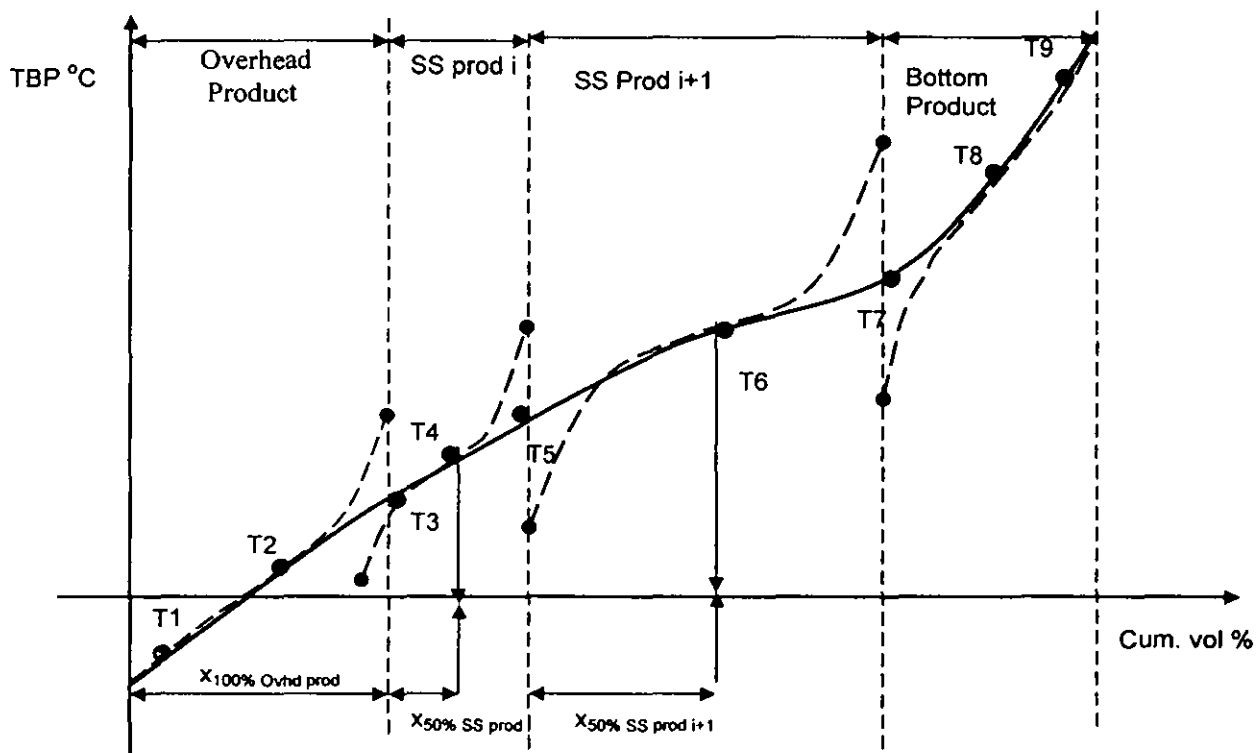


Figure 3.13 Reconstruction of Blended Feed TBP curve from Distillate products TBP curves

Step 3.3: Develop whole range blended feed TBP curve

Once TBP (X_{Feed}) points are determined, the whole range of TBP curve of blended feed is developed by using GDM. The algorithm to reconstruct Feed TBP curve from distillate product ASTM curves is summarised in Figure 3.14 below.

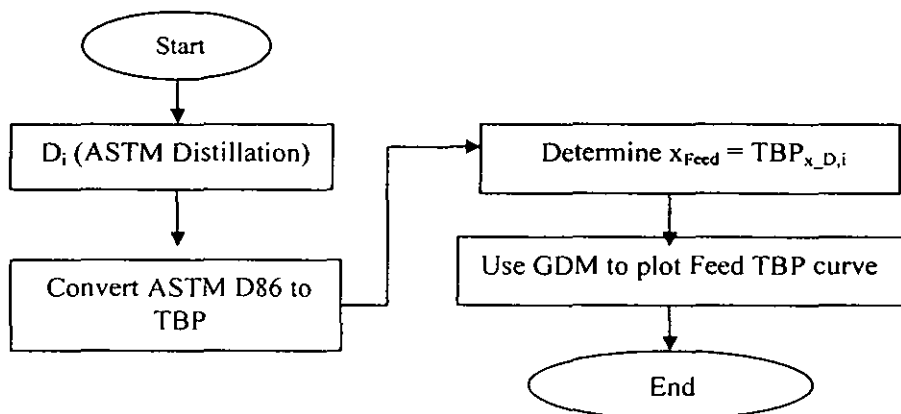


Figure 3.14 Algorithm for reconstruction Feed TBP curve from distillate products ASTM curve

Step 4: Reconstruction of SG distribution in blended feed

Procedure to Reconstruct SG distribution in blended feed:

Step 4.1: Calculate discrete cumulative volume fraction of distillate products

As mentioned in section 3.6, SG of all distillate products is referred to discrete cumulative fraction, x'_c . The fraction is calculated using equation 3.6

Step 4.2: Develop SG distribution curve

Once $SG_{D,i}$ (x'_c) are determined, *SG distribution curve* is developed by using GDM. The algorithm to reconstruct *SG distribution in Feed* from distillate product SG is given in figure 3.15.

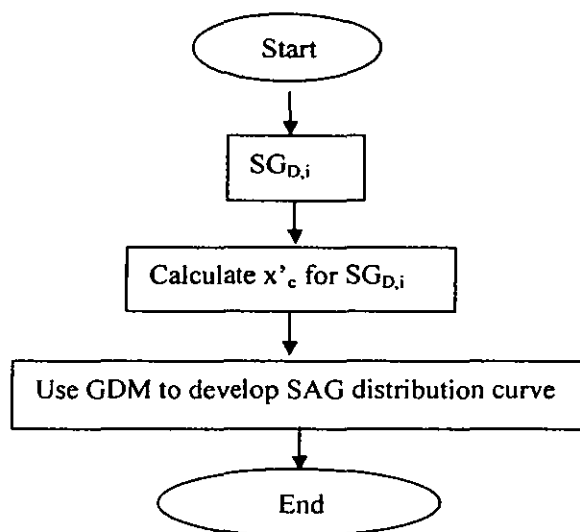


Figure 3.15 Algorithm for reconstruction SG distribution in pure condensate

Step 5: Calculate $M_{i,n}$ and $C_{i,n}$ of i^{th} pseudo component linear equations (Blended condensate)

In this step, the gradient $M_{i,n}$ and constant $C_{i,n}$ of i^{th} pseudo component of the blended condensates are calculated at α_n .

Step 6: Calculate $m_{i,j}$ and $C_{i,j}$ of i^{th} pseudo component linear equations (pure condensate)

Calculation of the gradient $m_{i,j}$ and constant $C_{i,j}$ of i^{th} pseudo component of the pure condensates requires simultaneous solution of i linear equations. Techniques such as Gauss elimination are applicable.

Step 7: Develop pure condensate TBP curve and SG distribution in pure condensate

Once the gradient m and constant c of the pure condensate linear equations are determined, the TBP and SG for the whole range of pure condensate can be developed.

3.6.1 Validation

The validation of the proposed procedure is carried out by comparing the predicted values against experimental values.

TBP curve of pure condensate

The TBP of pure condensates are analysed using SIMDIST (SD) method (ASTM D2887). This is a commonly used method to measuring boiling points of light hydrocarbon fractions. The conversion of SD to TBP can be done either using several methods such as Riazi-Daubert method, Daubert's method, or by simulation on process simulator.

Once the SD of pure condensates is converted to TBP, the values at respective cut points are compared against the predicted value using proposed model. The deviations are measured according to section 3.7.3.1.

SG distribution curve

The estimated values are compared against actual value. The deviation between the estimated and actual values is calculated using overall error square of the mixture bulk properties (E^2_p).

3.7 Desired product optimisation

There are several ways to perform optimisation, which among others is by using "Solver" of Excel. Each condensate that would give different distillate product yield even at the same cut points. Thus, optimization of the desired product yield can be determined by varying feed blending ratio as given in equating 3.33 below.

$$v_{D,\max} = \sum_{j=n}^j (v_{D,j})_{\alpha} \quad \dots\dots\dots \text{equation 3.33}$$

where V_D is the desired distillate product

j is type of condensate in the blended feed

α is feed blending ratio

In addition, the yield of distillate products is a function of its cut points as such it can be further enhanced by widening the boiling range. This can be done normally by adjusting the cut points i.e. changing the process variables of the column operating parameter e.g. reboiler temperature and reflux ratio.

From pure condensate TBP curve, the boiling range of each distillate products is determined and the potential yield of distillate product is calculated. By adopting swings cut method (Wenkai et al., 2007), the cut points are swing + 10°C and - 10°C, and the new yield of distilled product is calculated. This is illustrated in Figure 3.16:

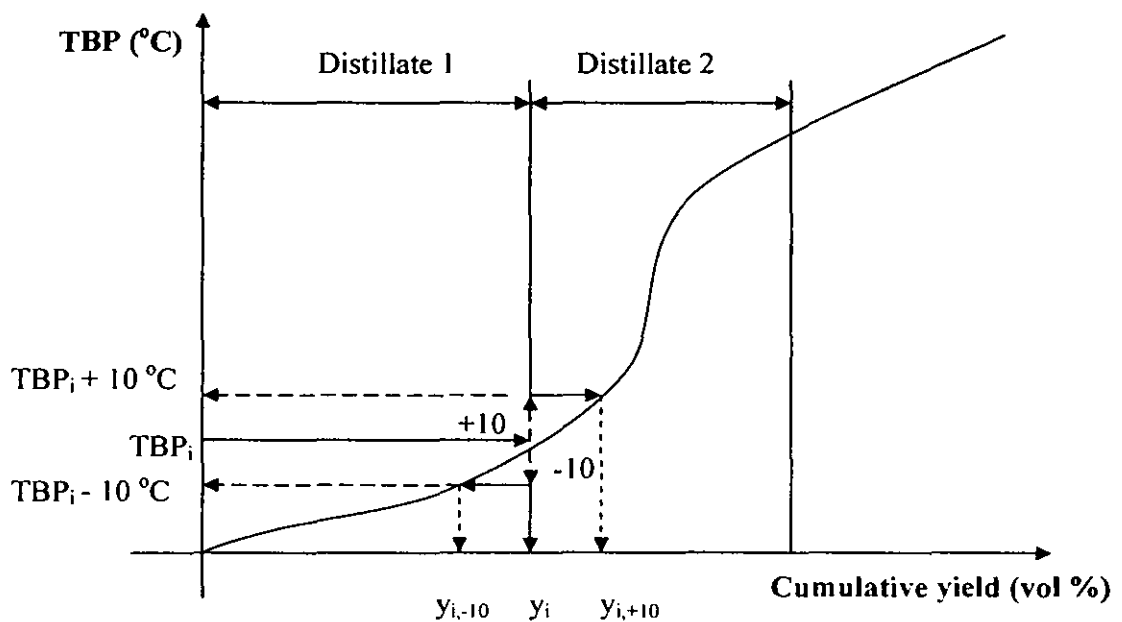


Figure 3.16 Swing cuts of product cut point

A composite PcLE model is developed in Excel using GDM. Thus, the desired product yield is optimized by varying the product's cut points and feed blending ratio. The objective function i.e. maximizing the desired product yield is therefore

determined at the optimal product cut points and feed blending ratio as defined by equation 3.34 below.

$$v_{D,max} = \sum_{j=n}^j (v_{D,j})'_\alpha \quad \dots\dots\dots \text{equation 3.34}$$

where $(V_D)'$ is the desired distillate product at different cut point.

The algorithm of optimization and swing cut method is illustrated in Figure 3.17:

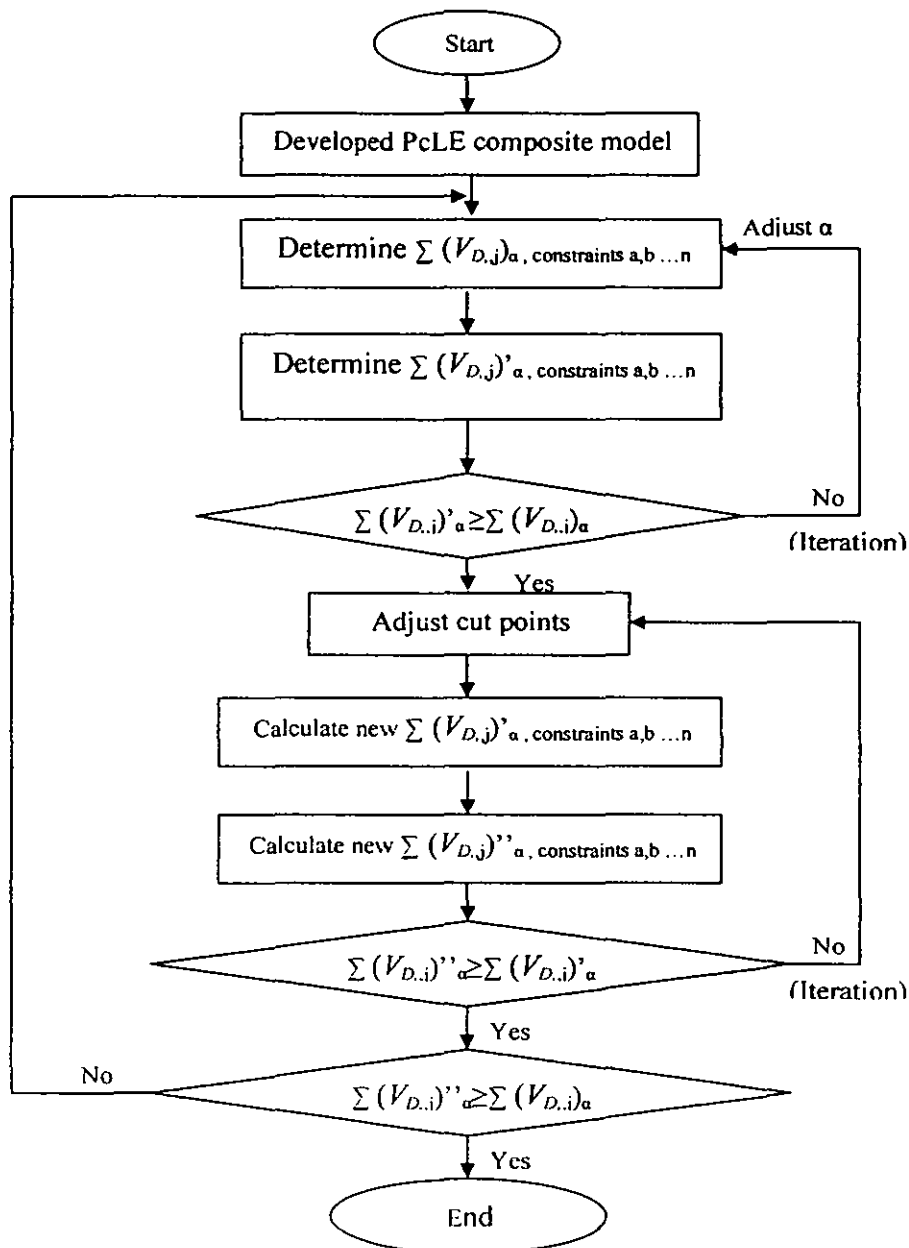


Figure 3.17 Algorithm of desired product optimisation

The steps taken for desired product optimisation is briefly described as follows:

Step 1: Develop PcLE composite model

From each PcLE of pure component, develop PcLE composite model using equation 3.34.

Step 2: Calculate maximum $(\sum V_{D,j})_{\alpha}$ at constraints a,b ...n

At defined boiling range of the desired distillate product and operating constraints such as top product limitation, use “solver” of Excel to determine the maximum yield by varying feed blending ratio, α . The maximum yield is determined by equation 3.35:

$$\sum (V_{D,j})'_{\alpha} \geq \sum (V_{D,j})_{\alpha} \dots\dots\dots \text{equation 3.35}$$

where $\sum (V_{D,j})_{\alpha}$ is the yield of desired distillate product of blended feed component $j=1, 2, 3, \dots, n$ at initial blending ratio, α and $\sum (V_{D,j})'_{\alpha}$ is the yield of desired distillate product of blended feed component $j=1, 2, 3, \dots, n$ at 1st iteration by adjusting the feed blending ratio, α .

Step 3: Calculate maximum $(V_{D,j})'_{\alpha}$ at different swing cuts

Adjust the upper and lower cut points of the desired distillate product by $+x$ °C and $-y$ °C respectively, and use “solver” of Excel to determine the maximum yield by varying x and y . Note that, the cut point swing shall be done within the acceptable limit of the desired product specifications. For Naphtha, the specifications shall be IP < 80 °C ASTM and EP < 180 °C ASTM.

The maximum yield at specific α is determined by equation 3.36:

$$\sum (V_{D,j})''_{\alpha} \geq \sum (V_{D,j})_{\alpha} \dots\dots\dots \text{equation 3.36}$$

where $\sum (V_{D,j})_{\alpha}$ is the yield of desired distillate product of blended feed component $j=1, 2, 3, \dots, n$ at original cut points, and $\sum (V_{D,j})''_{\alpha}$ is the yield of desired distillate product of blended feed component $j=1, 2, 3, \dots, n$ at 1st iteration, by adjusting the cut point.

Step 4: Select the optimum cut points and α

Compare $\sum (V_{D,j})'_\alpha$ and $\sum (V_{D,j})_\alpha$, and repeat step 2 at a new cut point, until the maximum volume fraction of the desired product yield is obtained.

3.8 Summary of methodology

In summary, spread sheet modelling were the main activities that involved predicting TBP curve and bulk properties distribution in blended using the selected methods. Process simulation using commercial software was performed only in the case where the empirical correlations methods cannot be used, for example the data used is beyond the allowable range. The overall research methodology involves in this study is summarised in Figure 3.18.

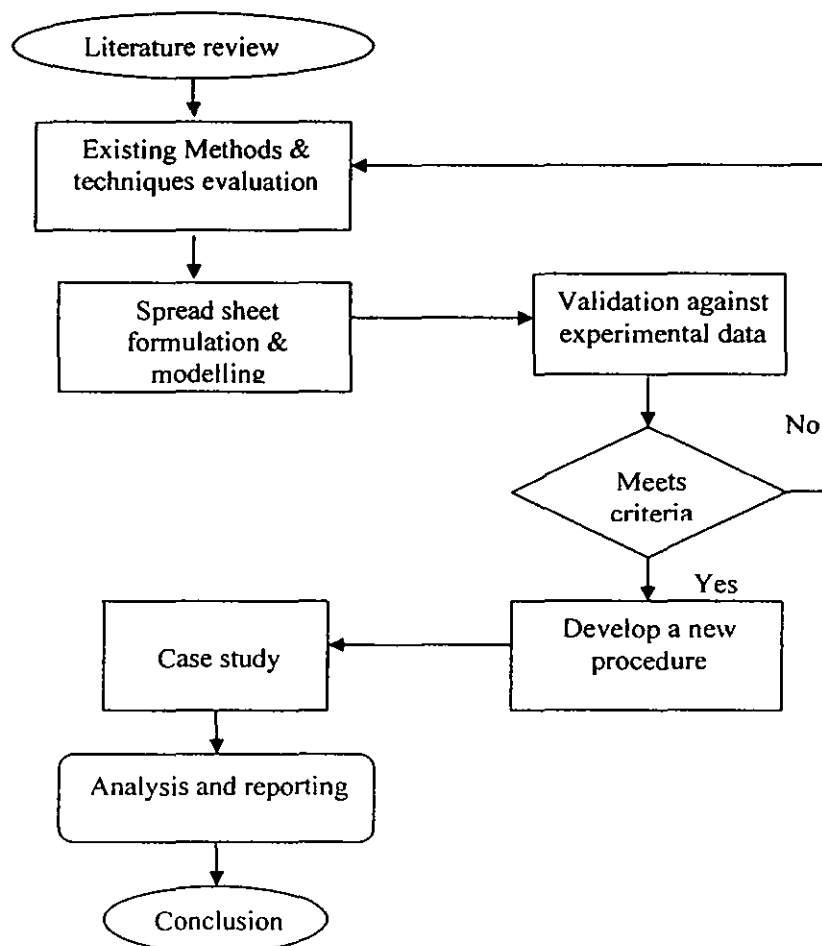


Figure 3.18 Overall research methodology

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Introduction

All the results obtained for the methodology and a case study are presented and discussed in this chapter.

4.2 TBP curve and bulk properties data for pure condensates

From the Bintulu (BNC) and Terengganu (TNC) condensate assays, only SG covers the whole cuts. However for Kinematic viscosity, K_{vis} only the cuts above 135°C are available. Consequently, the average value of K_{vis} within the boiling range of -5 to 135 °C is considered.

A summary of SG and K_{vis} for pure BNC and TNC are tabulated in table 4.1a and table 4.1b respectively.

Table 4.1a SG and K_{vis} of BNC at various volume fractions

TBP (°C)	vol fraction	cum vol _{ave} (%)	SG 60/60 F	K_{vis} @ 40°C	K'_{vis}
-5	0.00%	0	n/a	n/a	n/a
15	6.73%	3.36%	0.576	0.620	-4.245
70	32.24%	22.85%	0.654		
90	11.75%	44.85%	0.730		
135	22.94%	62.19%	0.760		
155	6.66%	76.99%	0.791	1.002	3.274
165	1.64%	81.14%	0.798		
175	2.04%	82.98%	0.803		
190	2.35%	85.18%	0.807	1.487	8.220
240	6.85%	89.78%	0.836	2.494	13.528
370	6.80%	96.60%	0.857	3.882	17.285
Overall			0.732	0.775	-0.493

Table 4.1b SG and K_{vis} of TNC at various volume fractions

TBP (°C)	Vol. fraction	cum vol. _{ave} (%)	SG 60/60 F	K_{vis} @ 40°C	K'_{vis}
-5	0	0.00%	n/a	n/a	n/a
15	5.17%	2.59%	0.5803	1.057	4.002
70	52.34%	31.34%	0.6443		
90	7.36%	61.19%	0.7196		
135	19.55%	74.65%	0.7501		
155	3.79%	86.32%	0.7798	1.202	5.668
165	1.30%	88.86%	0.7838		
175	1.49%	90.26%	0.7864		
190	1.30%	91.65%	0.7868	1.645	9.346
240	3.31%	93.96%	0.7991	2.584	13.853
370	4.39%	97.81%	0.836	4.059	17.631
overall			0.6942	1.150	5.105

4.3 Predicting results for pure condensates TBP-curves

In NCM, the cuts or pseudo-components shall be pre-determined; hence it is not practical or suitable to be used in predicting the blended condensate TBP curve. Therefore only GDM was used to predict blended TBP curve. Detail calculations are tabulated in Appendix 3. The predicted TBP curve at 0%, 25%, 50%, 75% and 100% of BNC in the blended condensates are shown in Figure 4.2a to 4.2e.

In general, the predicted TBP curves of the blended crude at various BNC:TNC blending ratio matches closely with the lab results, where the overall deviation is less than 1%. From the graph shown in Figure 4a to 4.2e, the deviation > 1% occurs at cumulative yield > 95% vol, except for 100% BNC, where the deviations > 1% are observed between cumulative yield 70 vol% - 80 vol% and 90 vol% - 95 vol%.

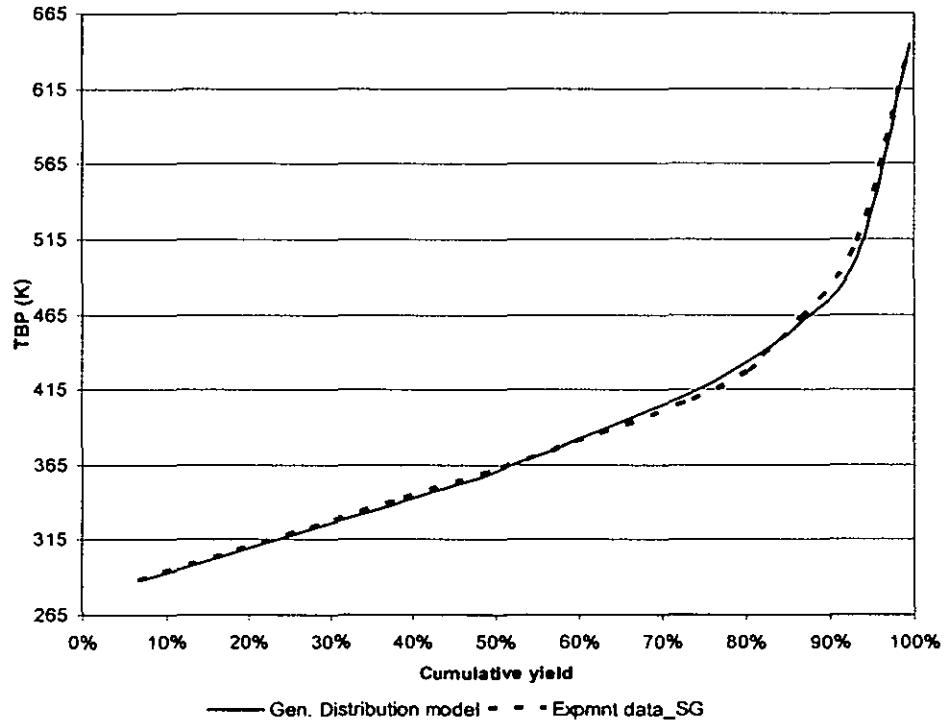


Figure 4.2a Predicted TBP curve of blended condensates at 100% BNC

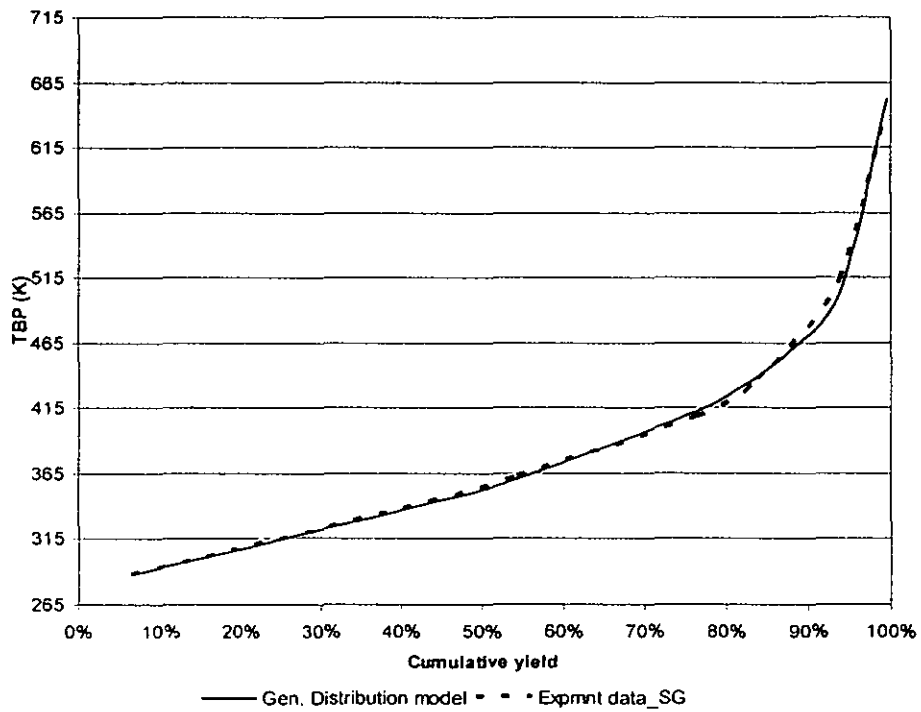


Figure 4.2b Predicted TBP curve of blended condensates at 75% BNC

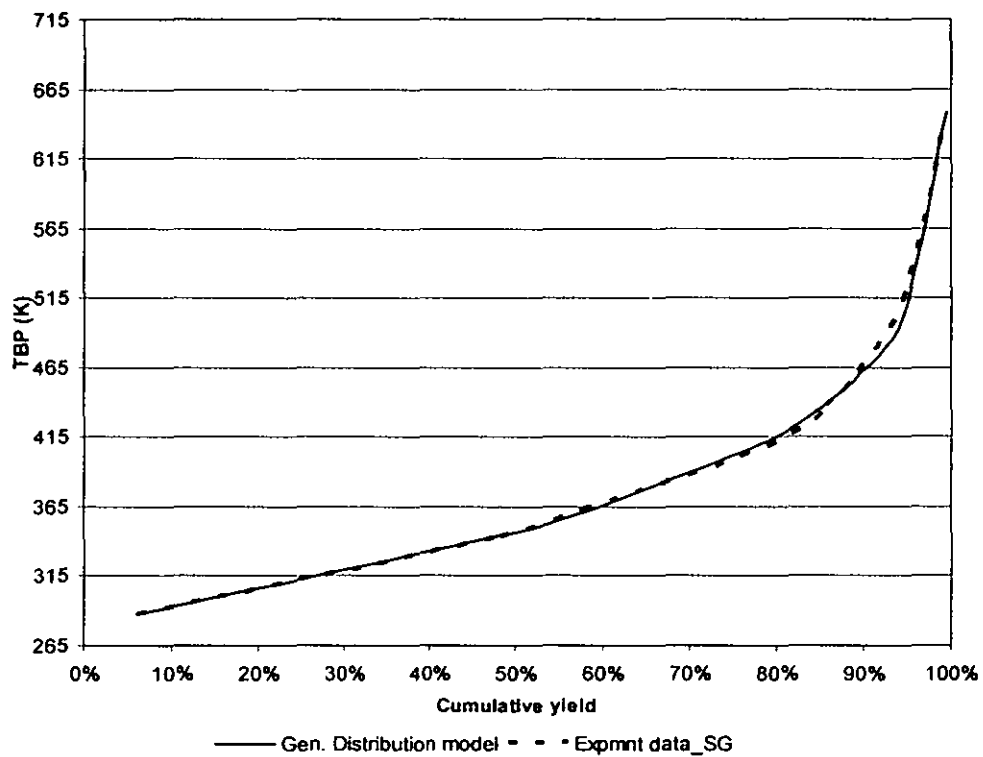


Figure 4.2c Predicted TBP curve of blended condensates at 50% BNC and 50% TNC

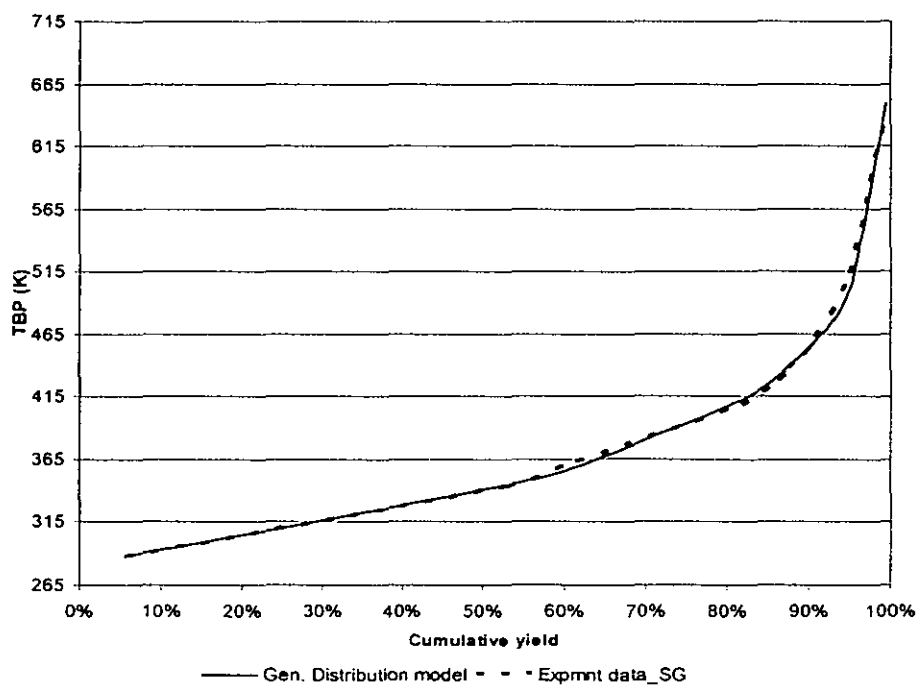


Figure 4.2d Predicted TBP curve of blended condensates at 25% BNC and 75% TNC

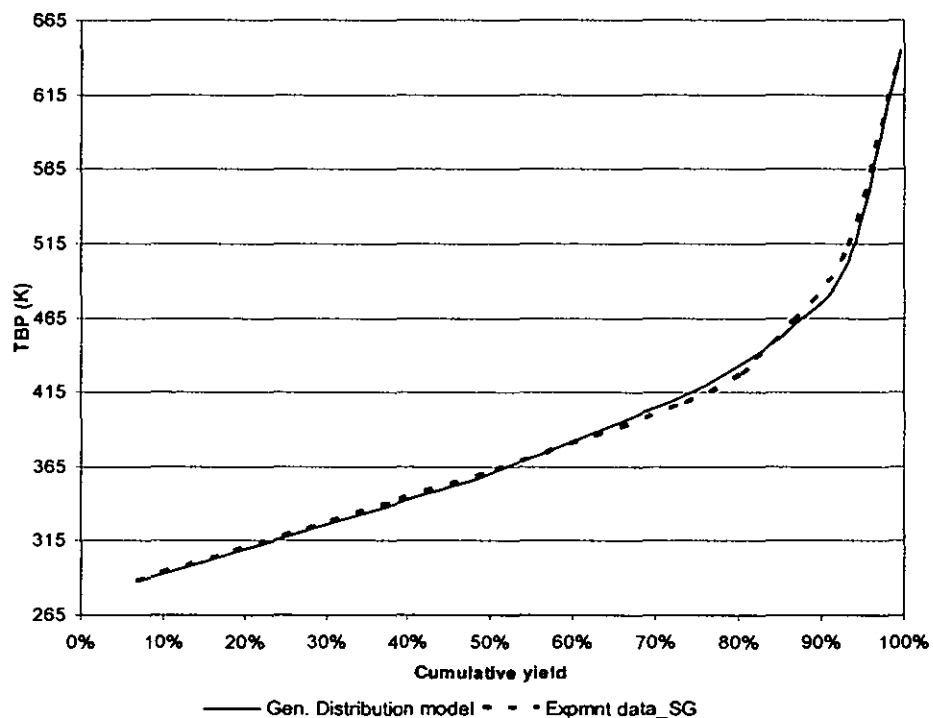


Figure 4.2e Predicted TBP curve of blended condensates at 100% TNC

The summary of %AAD at various blending ratio is given in Table 4.2a.

Table 4.2a %AAD of predicted TBP curve at various feed blending ratios

BNC in Blended condensates (%)	% AAD
0	0.88%
25	0.83%
50	0.76%
75	0.77%
85	0.68%
100	0.72%

The results showed that GDM gives excellent predicting as shown in Figure 4.2a – 4.2e, where the model can be used to predict accurately blended condensates TBP curve at various blending ratio with % AAD < 1%.

4.4 Predicting results of SG & K_{vis} distribution in blended condensates

In this case, both GDM and NCM were used to predict SG and K_{vis} distribution in blended condensates. Detail calculations are tabulated in Appendix 4.

4.4.1 Predicting results of SG distribution in blended condensates

The graph of predicted SG distribution versus experimental results at 0%, 25%, 50%, 75% and 100% of BNC in the blended condensates are shown in Figure 4.3.1a to 4.3.1e.

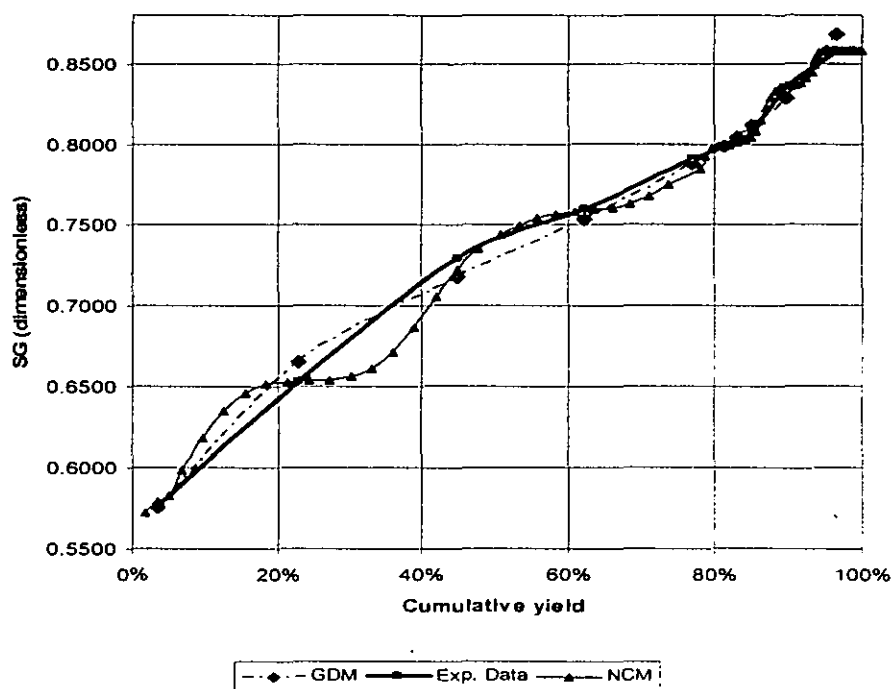


Figure 4.3.1a Predicted SG distributions in blended condensates at 100% BNC

Figure 4.3.1a shows “helical” trend of predicted SG using both GDM and NCM. The predicted SG curve using GDM intercepted with the experiment curve at four points, mostly at 80% - 100% cumulative yield. For NCM, predicted SG curve intercepted with the experiment curve at all points that closer to wide cuts where larger deviation occurs at the mid point of the wide cuts. The deviations measured at each wide cuts indicate that GDM gives deviation range from -0.9% to $+1.8\%$ while NCM gives smaller deviation i.e. $< 0.5\%$ except at cumulative yield 3.36%.

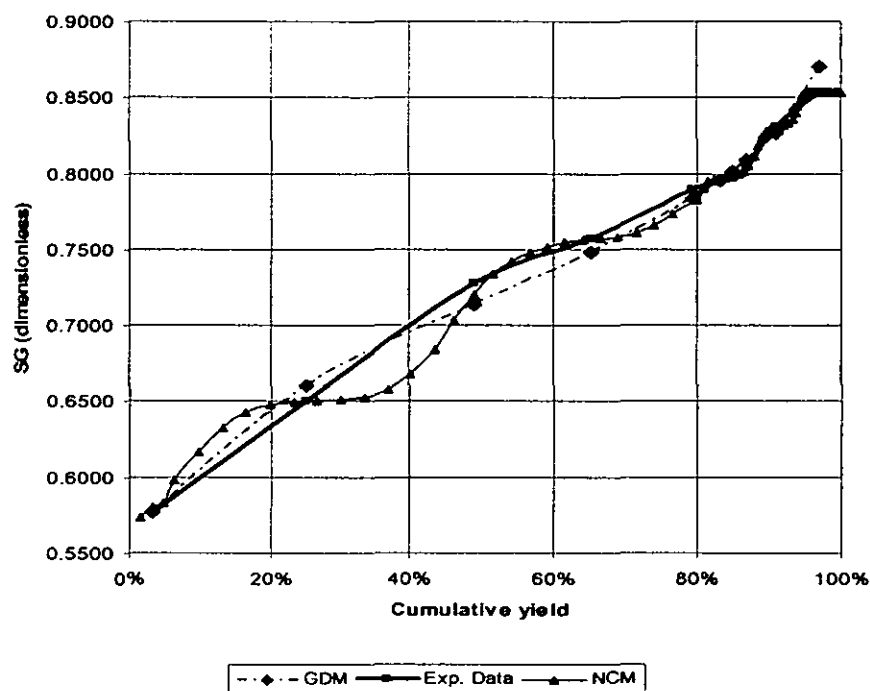


Figure 4.3.1b Predicted SG distributions in blended condensates at 75% BNC

Figure 4.3.1b also showed similar “helical” trend of predicted SG using both GDM and NCM. The predicted SG curve using GDM intercepted with the experiment curve at higher cumulative yields. The deviations measured at each wide cuts indicate that SG predicted by GDM gives deviation range from -2% to $+2\%$. NCM again gives smaller deviation i.e. $< 0.5\%$ except at cumulative yield 3.36%.

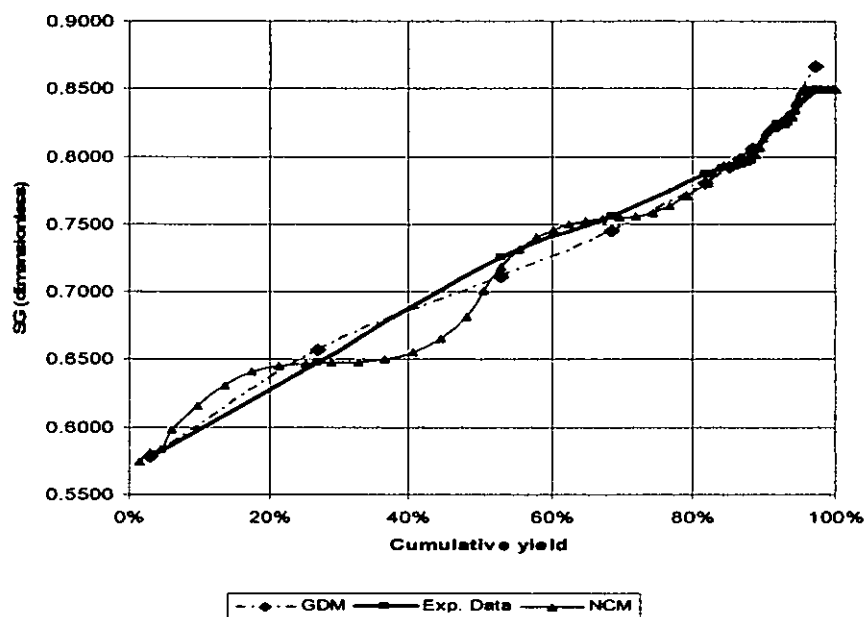


Figure 4.3.1c Predicted SG distributions in blended condensates at 50% BNC

Similar trend is observed in Figure 4.3.1c where for GDM, the intercepting points are shifted to the right side. The deviations measured at each wide cuts indicate that GDM gives deviation range from -2% to $+2.12\%$. NCM gives smaller deviation i.e. $< 0.5\%$ except at cumulative yield 3.36%.

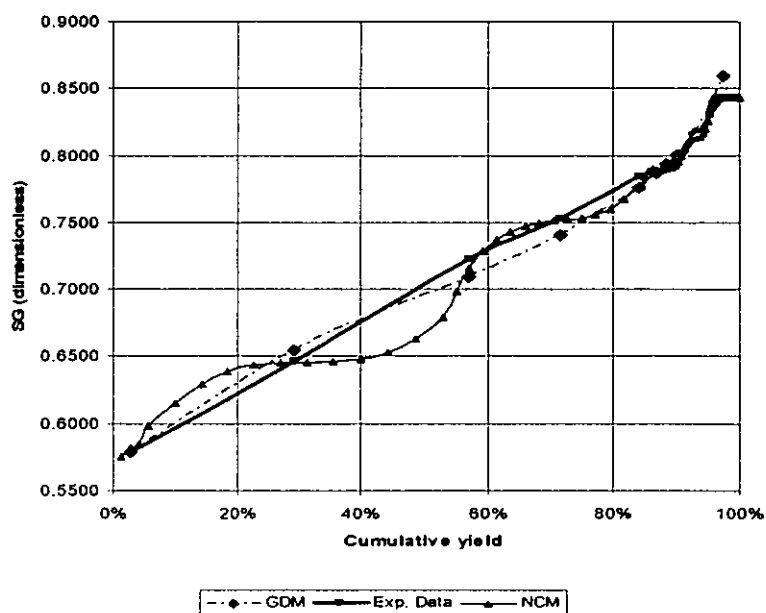


Figure 4.3.1d Predicted SG distributions in blended condensates at 25% BNC

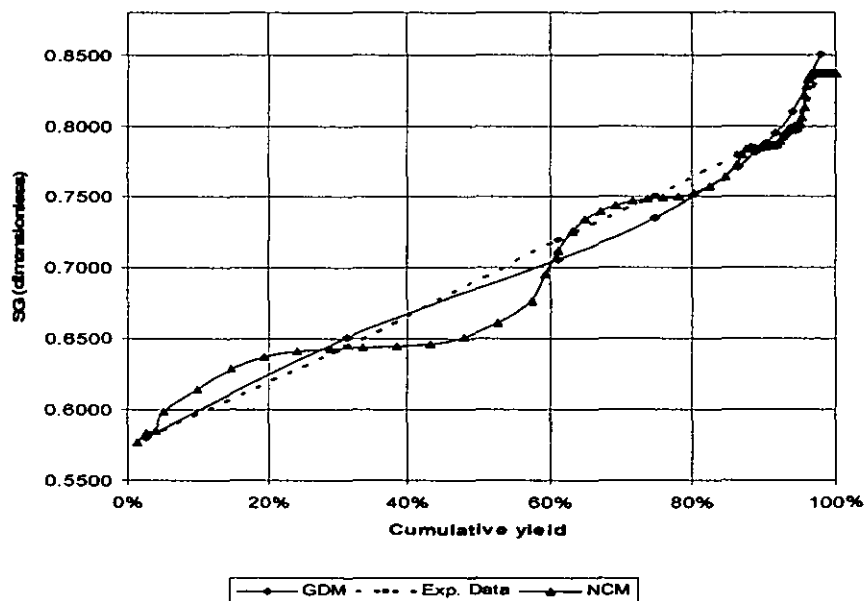


Figure 4.3.1e Predicted SG distributions in blended condensates at 100% TNC

Figure 4.3.1d and 4.3.1e also show similar trend for the predicted SG distribution curves, where the intercepting points for GDM are further shifted to the right side.

A summary of %AAD and E^2 of SG distribution in blended BNC-TNC at various blending ratio are given in Table 4.3a and Table 4.3b.

Table 4.1.3(a) %AAD of SG distribution in blended condensates at various blending ratios

% of BNC	% AAD	
	GDM	NCM
0%	1.08%	0.21%
25.00%	0.94%	0.22%
50.00%	0.90%	0.24%
75.00%	0.88%	0.25%
85.00%	0.85%	0.25%
100.00%	0.79%	0.26%

Table 4.1.3(b) E^2 of SG distribution in blended condensates at various blending ratios

% of BNC	E^2 for whole range mixtures	
	GDM	NCM
0%	0.0011%	0.0011%
25% BNC	0.0014%	0.0021%
50% BNC	0.0030%	0.0034%
75% BNC	0.0051%	0.0050%
85% BNC	0.0057%	0.0057%
100% BNC	0.0069%	0.0067%

The error analysis results from Table 4.1(a) and (b) showed that both GDM and NCM are capable of predicting SG distribution in blended condensates with good accuracy based on %D and %AAD calculated at each wide cuts. However, NCM gives bigger deviations than GDM if SG at narrow cuts were considered in the calculation. This is due to “helical” trend of the predicted SG curve where it is intercepting with experimental curve at all points nearer to wide cuts with larger deviation occurred at their mid points as shown in Figures 4.3.1(a) to (e).

4.4.2 Predicting results of K_{vis} distribution in blended condensates

The graph for predicted K_{vis} distribution at 0%, 25%, 50%, 75% and 100% of BNC in the blended condensates are shown in figure 4.3.2a to 4.3.2e. The details are given in Appendix 4.

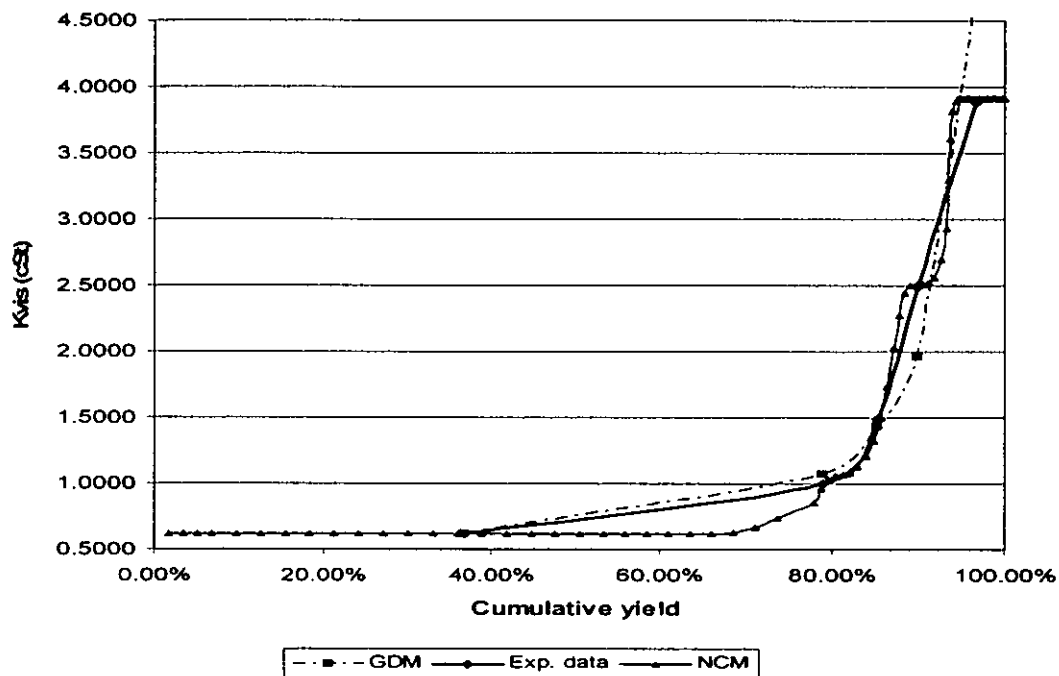


Figure 4.3.2a Predicted K_{vis} distributions in blended condensates at 100% BNC

Figure 4.3.2a shows “helical” trend of predicted K_{vis} using NCM. The predicted K_{vis} curve using GDM intercepted with the experiment curve at two points while NCM, the predicted SG curve intercepted with the experiment curve at all points that closer to wide cuts where larger deviation occurs the mid point of the wide cuts. The deviations measured at each wide cuts indicate that GDM gives deviation $> 20\%$ at cumulative yield 89% onward. NCM gives smaller deviation i.e. $< 0.5\%$ except at cumulative yield 85%.

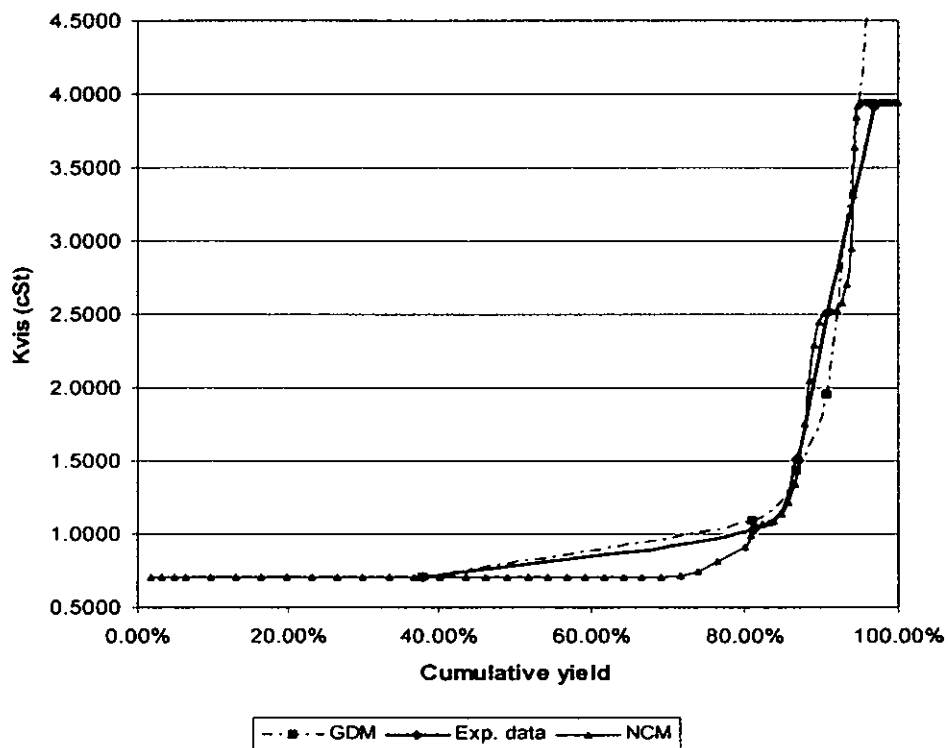


Figure 4.3.2b Predicted K_{vis} distributions in blended condensates at 75% BNC

Similar trends are observed for the predicted K_{vis} distributions in blended condensates at various blending ratio as shown in Figures 4.3.2(b) to (e) i.e. the deviations measured at each wide cuts indicate that GDM gives deviation > 20% at cumulative yield 90% onward while NCM gives smaller deviation i.e. < 1%.

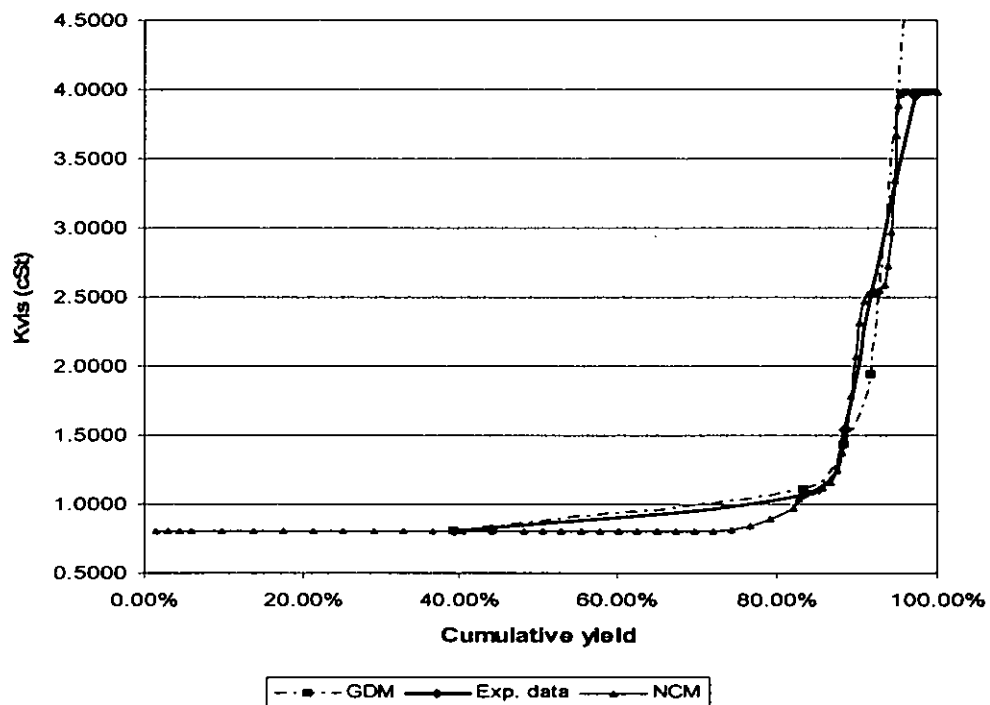


Figure 4.3.2c Predicted K_{vis} distributions in blended condensates at 50% BNC

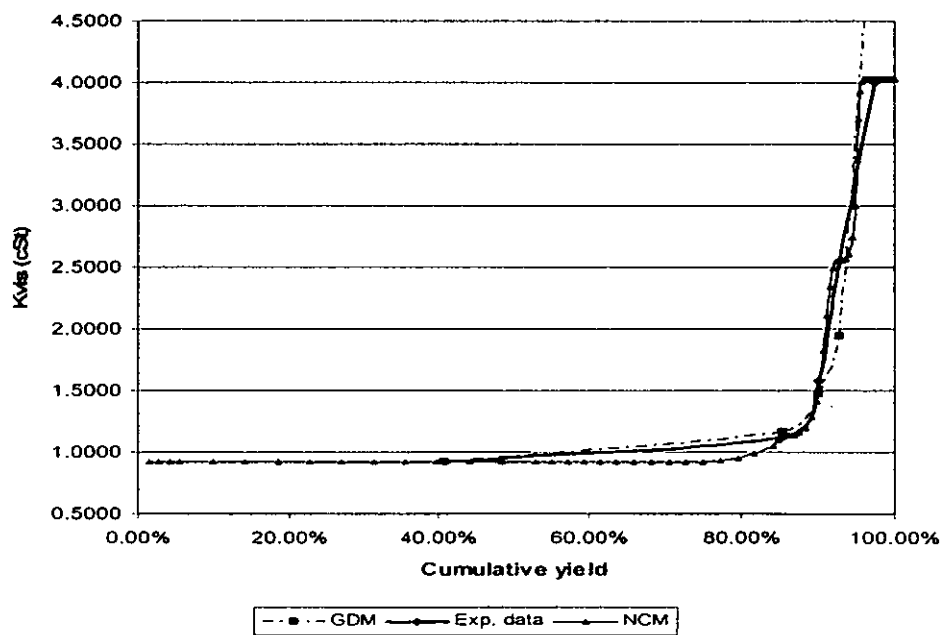


Figure 4.3.2d Predicted K_{vis} distributions in blended condensates at 25% BNC

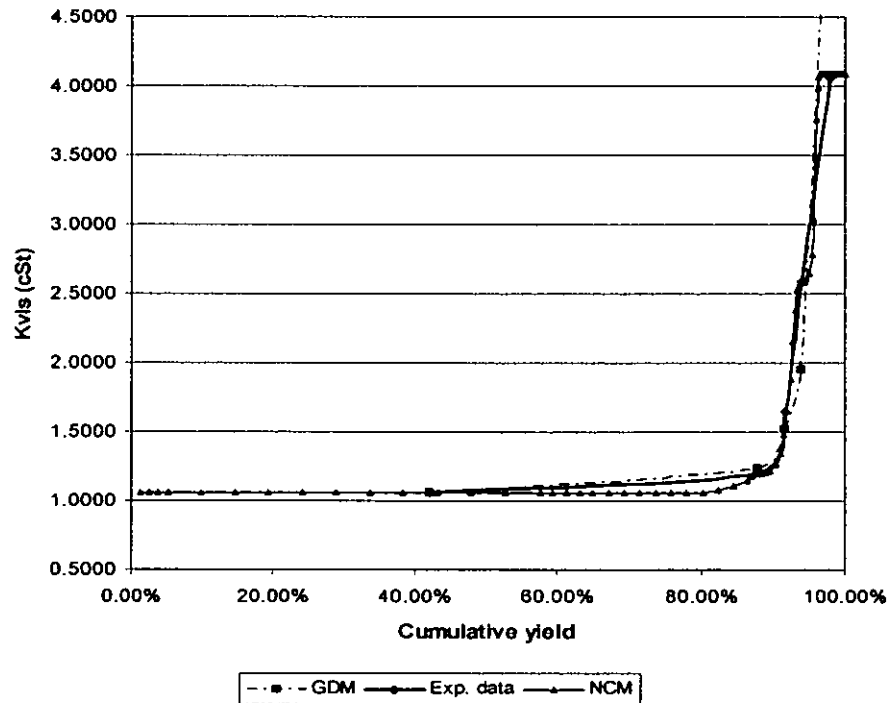


Figure 4.3.2e Predicted K_{vis} distributions in blended condensates at 100% TNC

A summary of %AAD and E^2 of K_{vis} distribution in blended BNC-TNC at various blending ratio are given in Table 4.3.2a and (b):

Table 4.3.2(a) %AAD of predicted K_{vis} distribution at various blending ratios

% of BNC	AAD	
	GDM	NCM
0 %	16.252%	0.336%
25 %	14.304%	0.290%
50 %	13.752%	0.328%
75 %	11.673%	0.463%
85 %	10.880%	0.526%
100 %	10.418%	0.627%

Table 4.3.2(b) E^2 of SG distribution at various blending ratios

% of BNC	E^2 for whole range mixtures	
	GDM	NCM
0 %	0.00110%	0.00003%
25 %	0.00047%	0.00002%
50 %	0.00022%	0.00004%
75 %	0.00017%	0.00007%
85 %	0.00021%	0.00008%
100 %	0.00025%	0.00010%

The error analysis results shown in Table 4.3.2(a) indicates that GDM predicts K_{vis} distribution in blended condensates with considerable error compared to NCM. However, the error given by NCM would be higher if K_{vis} at narrow cuts were considered in the calculation. This is due to “helical” trend of the predicted K_{vis} curve that intercepting with experimental curve at all points nearer to wide cuts with larger deviation occurred at their mid points as shown in Figure 4.3.2(a) to (e).

4.5 Model validation

Model validation was conducted for pure BNC. The feed and distillate products volumetric flow rate at $\alpha = 1$ (pure BNC) is given in Table 4.4.1a. Since predicted K_{vis} gave high deviation when predicting using GDM, therefore only TBP and SG were considered in this study for model validation. Furthermore TBP and SG are the prominent parameters for crude oil and petroleum fraction characterisation, where their correlations give the most accurate estimation of other bulk properties. ASTM distillation and SG for all distillate products are given in Table 4.4.1b.

The top product of Condensate Fractionating column is volatile and therefore it is impossible to perform ASTM distillation. It feeds into Condensate Stripper where about 10% leaves the column as its top product. For simplicity, the ASTM distillation of the bottom product of Condensate Stripper is used to represent Condensate Fractionating column top product. The conversion of ASTM D86 to TBP was done

using Daubert's method for all distillate products and the results are shown in table 4.4.1a.

Table 4.4.1a ASTM conversion to TBP for all distillate products

vol (%)	Top product (38.64 % vol)		Naphtha (37.36 % vol)		Bottom product (24 % vol)	
	ASTM D86 (°C)	TBP-Daubert (°C)	ASTM D86 (°C)	TBP-Daubert (°C)	ASTM D86 (°C)	TBP-Daubert (°C)
0.5	31	8.21	82.7	55.93	116.7	77.42
10	38	27.13	92.5	79.10	143.7	120.08
30	40.9	36.02	97.5	92.24	167.4	160.14
50	44.5	43.54	103.8	104.01	193.9	197.33
70	50.8	53.83	114.4	119.78	225.9	236.33
90	64.7	73.04	138.1	148.52	273.5	285.00
100	76.4	81.38	175.1	204.91	348	465.28

TBP of distillate products at their specific volume fraction used to reconstruct Feed TBP curve are summarised in Table 4.4.1b.

Table 4.4.1b Feed TBP at specific volume fraction of Distillate products

X_i , Distillate i	$TBP_{D,i}$ (°C)	X_{feed}	TBP_{Feed} (°C)
Top Prod_10%	27.13	0.04	27.13
Top Prod_30%	36.02	0.12	36.02
Top Prod_50%	43.54	0.20	43.54
Top Prod_EP	81.38	0.38	-
Top Prod / Naphtha cut point	68.66	0.375	68.66
Naphtha_IP	55.93	0.37	-
Naphtha_50%	104.01	0.57	104.01
Naphtha / Bot prod cut point	150.67	0.76	141.16
Bot Prod_50%	197.33	0.88	197.33
Bot Prod_90%	285.00	0.976	285.00

By using GDM, the whole range Feed TBP curve is developed and is shown in Figure 4.4.1a.

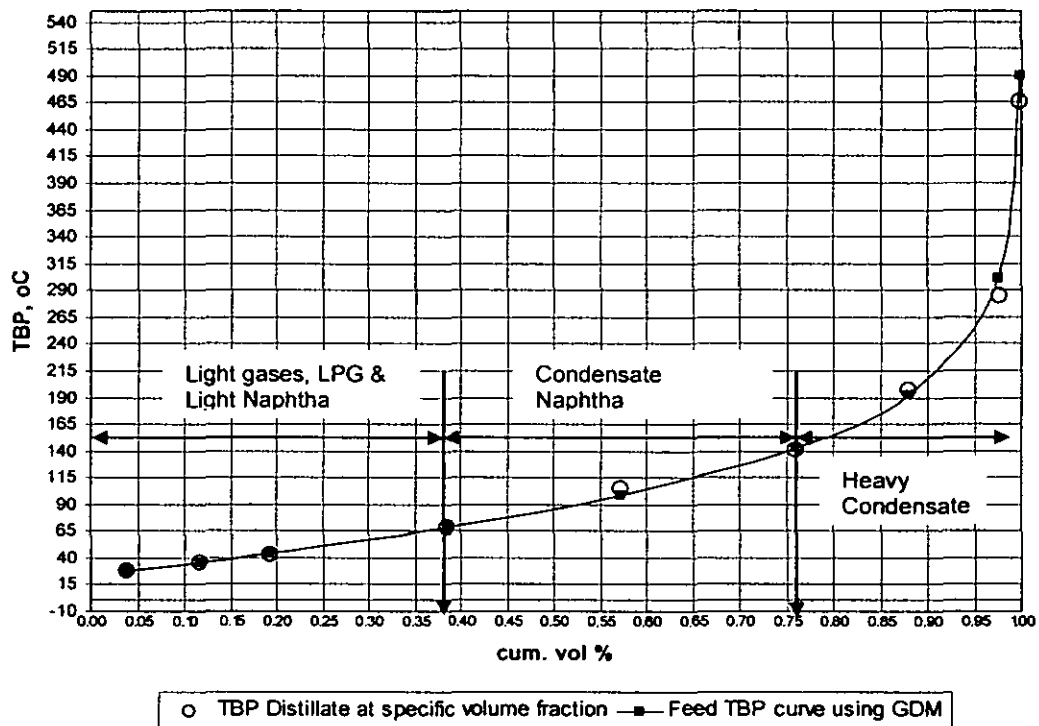


Figure 4.4.1a Reconstructed Feed TBP curve using GDM

The actual sample of pure BNC was analysed using ASTM D2887 method where the result was reported in SIMDIST (SD). SD is converted to TBP using AspenHYSIS™ v3.1 instead of using Daubert's method because ΔT_{SD} of the adjacent cuts exceeds the limit specified in Daubert's method. The reconstructed, actual and original lab data (crude assays) of Feed TBP curves are shown in Figure 4.4.1b.

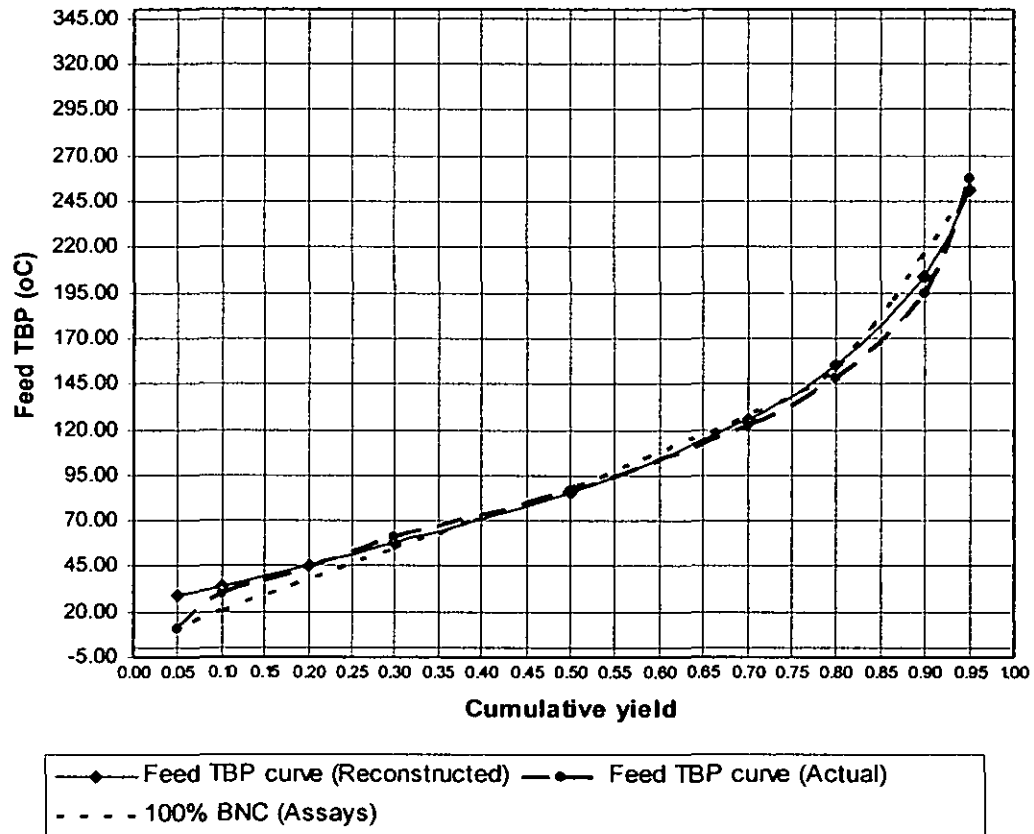


Figure 4.4.1(b) Predicted and actual Feed TBP curves

Figure 4.4.1(b) shows that the BNC's TBP curve, sampled taken in year 2008 has deviated from its crude assays reported in year 2002.

For model validation purposes, only the deviations between the reconstructed Feed TBP curve and the actual Feed TBP curve were calculated. By using parity plot method, the coefficient R^2 is determined. In this study, only the predicted TBP at cumulative yield ranging from 10% to 95% are considered. This is mainly because higher inaccuracy is expected below and above this range due to difficulties to sample and analyse the light gas and heavy condensate fractions. A parity plot between the predicted values of the Feed TBP curve and the experimental data is shown in Figure 4.4.1(c).

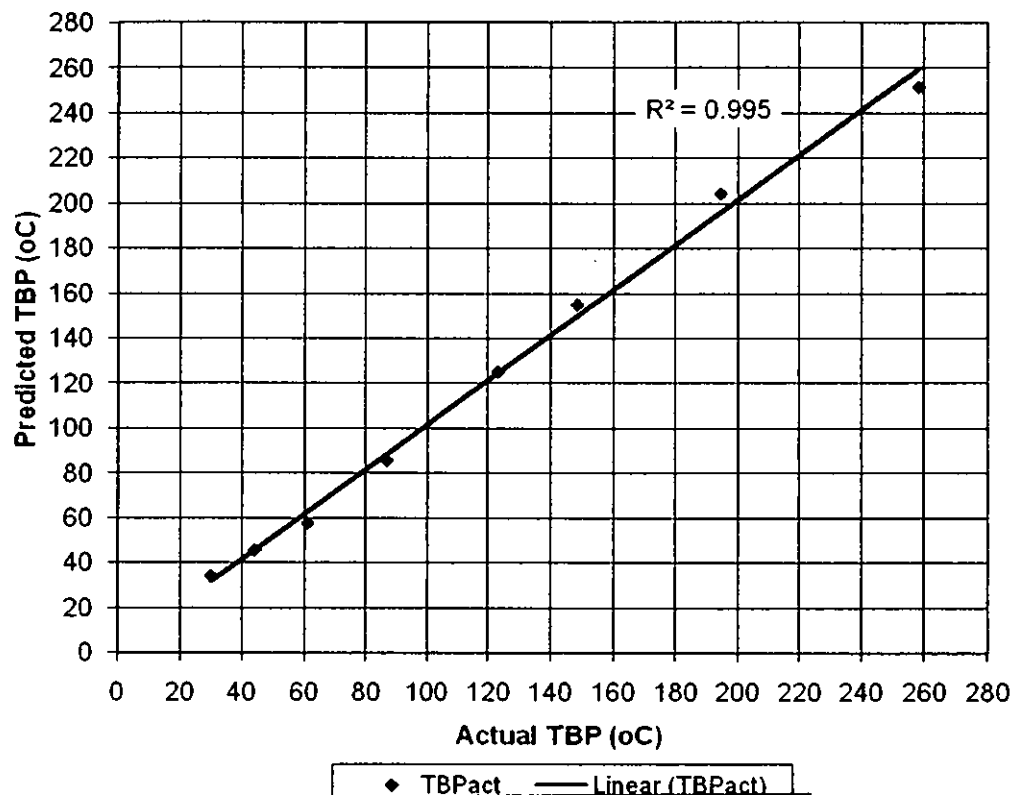


Figure 4.4.1(c) Comparison of predicted TBP curve with experimental data

From the graph, the coefficient R^2 is 0.995 which is sufficiently good. The biggest deviation occurs at cumulative yield 10 vol% where the deviation is +14.5%. Higher Δ TBP between model and actual at this cumulative yield is expected, it is because the model was developed based on Condensate Stripper bottom product. In actual fact, top product of Condensate Fractionator might contain light gases and LPG where these gases are removed from Condensate Stripper as bottom product. Table 4.4.2a shows SG of distillate products used to predict SG distribution in BNC.

Table 4.4.2a SG of Distillate product at average cum. vol.%

	cum vol %	cum vol _{ave} (%)	SG _{Feed}
Top prod	38.64%	19.32%	0.655
Naphtha	37.36%	57.32%	0.757
Bottom prod	24%	88.00%	0.820

By using GDM, the SG distribution in BNC is developed and is shown in figure 4.4.2a.

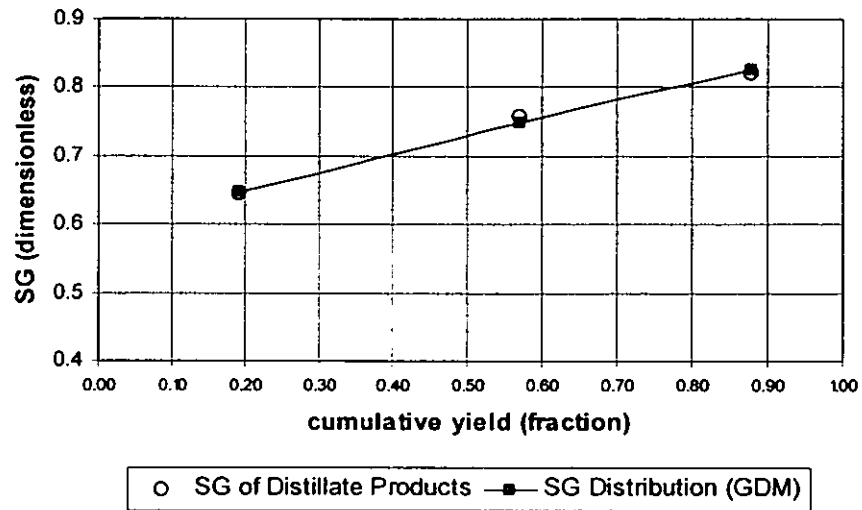


Figure 4.4.2a SG distribution in Feed using GDM

Since the actual data for SG distribution in BNC is not available, the results were compared against crude assays data. The predicted SG and original lab data (crude assays) SG distributed in BNC are shown in figure 4.4.2b below.

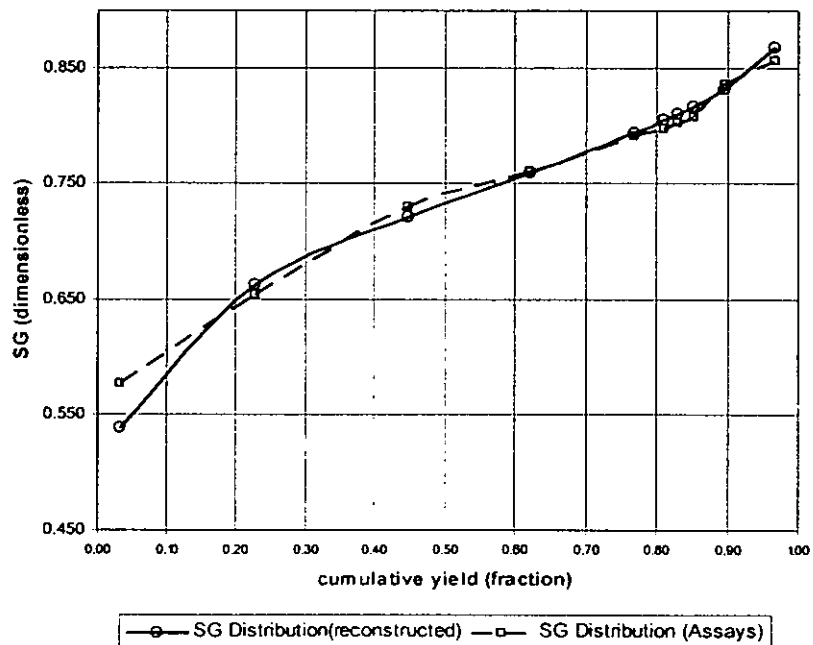


Figure 4.4.2(b) Predicted and actual Feed SG curves

The coefficient R^2 is determined in parity plot between the predicted values of the SG and experimental value as shown in Figure 4.4.2c.

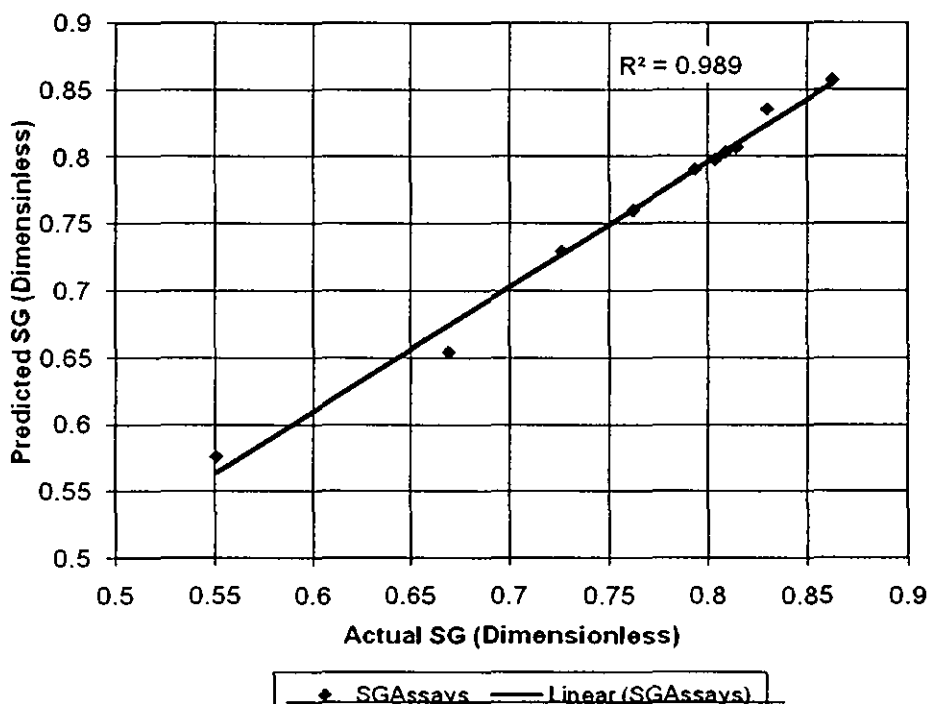


Figure 4.4.2c Comparison SG distribution – Reconstruction & Assays

From the graph, the coefficient R^2 is 0.989 which is sufficiently good. The biggest deviation occurs at cumulative yield 3.36 vol% where the deviation is -4.3%. The reason for large ΔSG between model and actual at this cumulative yield mostly because the model was developed based on the data of Condensate Stripper bottom product where light gases and LPG in Condensate Stripper overhead product. The deviations of the predicted SG distribution in BNC against original SG are tabulated in Appendix 4.

4.6 A Case Study

A case study was carried out on Condensate Tower of Condensate Fractionating Unit (CFU) of local refinery. The distillation column was fed with two Malaysian condensate; Bintulu Condensate (BNC) and Terengganu Condensate (TNC) where these condensates were blended prior to feeding into the distillation column. The column operates slightly above the atmospheric pressure to distil top product, Heavy Naphtha as side stream product and heavy condensate as bottom product. The top product is send to Condensate Stabiliser to separate light gases plus LPG from Light Naphtha. The bottom product is send to Crude Distillation unit (CDU) where it is mixed with crude oils prior to entering the Atmospheric Distillation Column of CDU. Figure 4.4.2d below shows a schematic diagram of CFU.

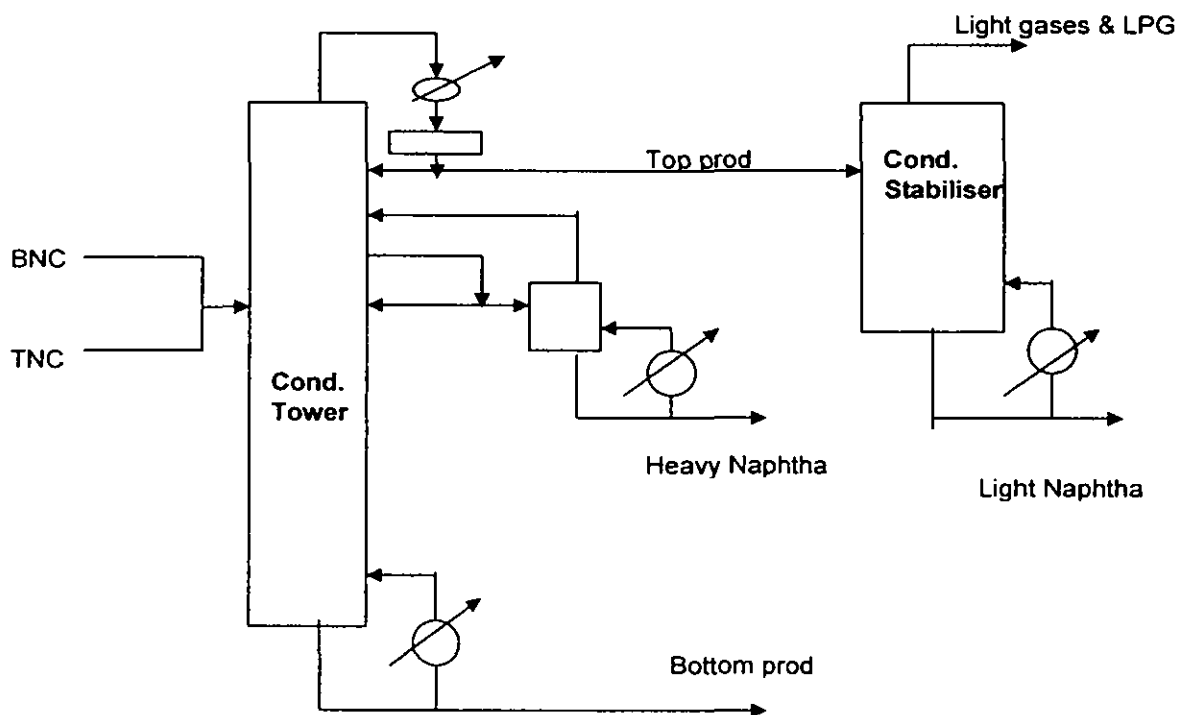


Figure 4.4.2d Simplified Schematic Diagram of CFU

At present the feed to Condensate Tower is either 100% BNC or 50:50 ratios of BNC and TNC. Feed samplings are normally carried out for new condensates loading. Sample of distillate products are taken and analysed on weekly basis.

4.6.1 Case study Outline Procedure

The procedure in section 3.9.1 was used in a case study to predict pure condensate TBP curves. The procedure was developed based on readily available information from plant databank system. It means that all the required information are solely taken from normal plant operation routines sampling and lab analysis activities i.e. no additional lab analysis would be carried out except for model validation purposes.

Top Product of Condensate Tower contains light hydrocarbon where the lab analysis is performed using Gas Chromatograph (GC) on percentage evaporated (%Eva) while the rest of distillate products including Condensate Stabiliser Bottom are using ASTM D86 method where the percentage recovered is measured against boiling temperature. For simplification and consistency, ASTM distillation data for Condensate Stabiliser bottom product is used for Condensate Tower Top Product. However, SG is still refers to top product of Condensate Tower. This is because only 10% of the total distillate products from Condensate Stabiliser will go as overhead product where the remaining will go as bottom product, as shown in figure 4.4.2e. This small amount of overhead product that comprises of light gases and LPG will not affect so much the reconstruction of Feed TBP curve and therefore it can be ignored.

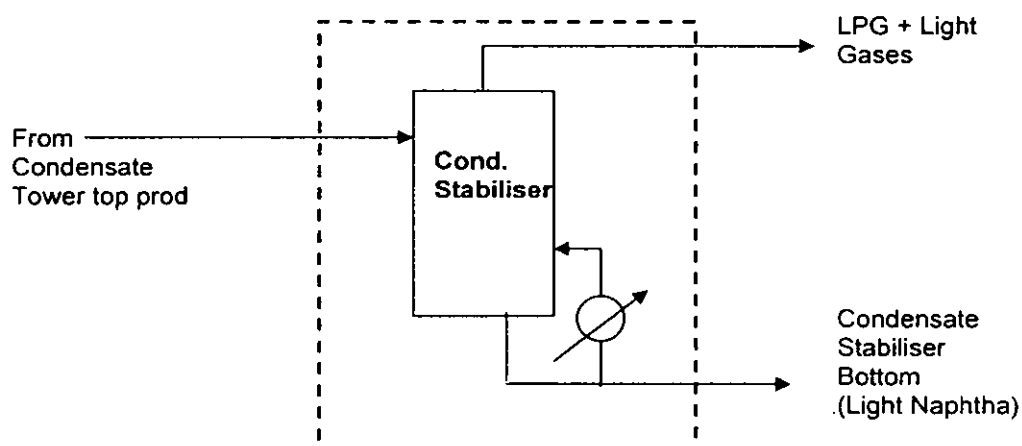


Figure 4.4.2e Mass Balance around Condensate Stabiliser Column

4.6.2 Prediction of pure condensates TBP curve using Hybrid GDM-PcLE method

The feed and distillate products volumetric flow rates at different feed blending ratio, α , and the conversion of ASTM distillation to TBP for distillate products was carried out using Daubert's method are shown in Appendix 5.

The whole range Feed TBP curve at $\alpha = 0.5$ and $\alpha = 1$ were developed using GDM. The reconstructed Feed TBP curves are shown in figure 4.4.3(a) and figure 4.4.3(b) respectively.

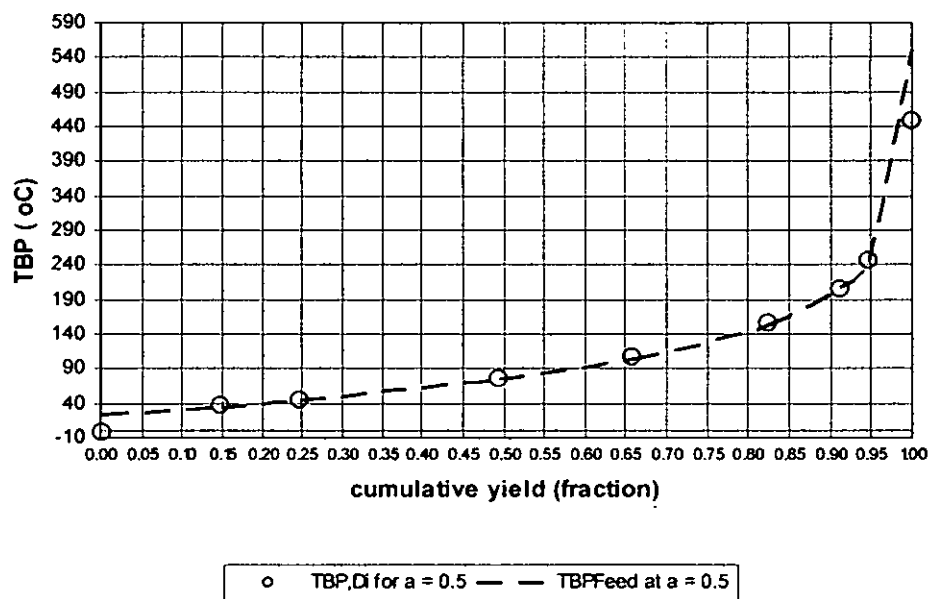


Figure 4.4.3a Feed TBP curve for $\alpha = 0.5$ using GDM

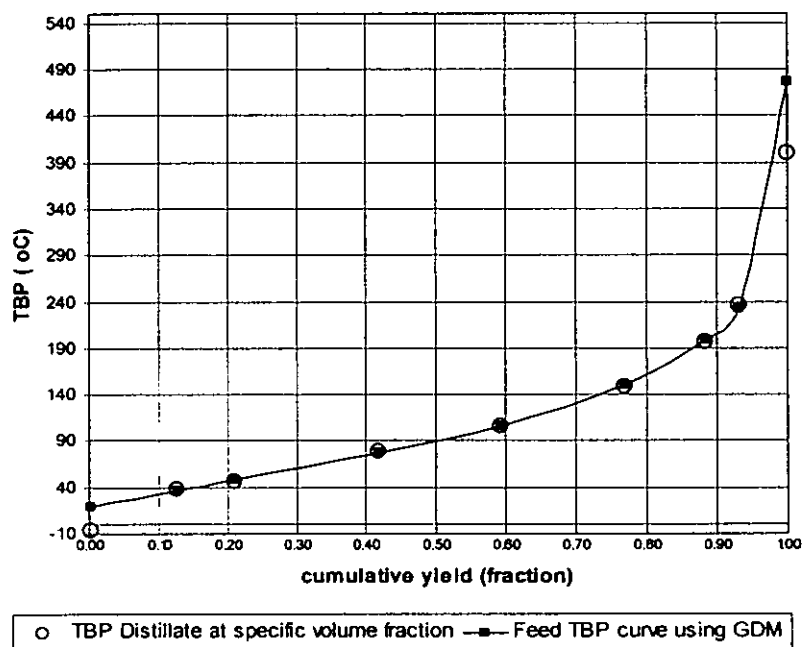


Figure 4.4.3b Feed TBP curve $\alpha=1$ using GDM

The whole range Feed TBP curve was split into pseudo-components each with 10 °C boiling range. The gradient m and constant c of linear equation for each pseudo-component at $\alpha=0.5$ and $\alpha=1$ were calculated. The calculations are given in Appendix 5.

Note that for 100% TNC, $\alpha=0$. The slope m and intersect c of each linear pseudo component equations at $\alpha=0$ determined using Gauss method. The results are shown in table 4.3.

Table 4.4.3 The slope m and intersect c of each TBP's PcLE at various α

TBP (°C)	$\alpha = 0.5$			$\alpha = 1$			$\alpha = 0$		
	x_i	m	c	x_i	m	c	x_i	m	c
25.0	2.57%	0.0124	-0.43011	3.88%			1.26%		
30.0	8.75%	0.0113	-0.43011	7.39%	0.0124	-0.2834	10.11%	0.0070	-0.1366
40.0	20.01%	0.0099	-0.34797	14.96%	0.0113	-0.2502	25.08%	0.0075	-0.1524
50.0	29.90%	0.0087	-0.23343	22.67%	0.0099	-0.1957	37.19%	0.0077	-0.1579
60.0	38.58%	0.0076	-0.12215	30.18%	0.0087	-0.1351	47.07%	0.0075	-0.1482
70.0	46.20%	0.0067	-0.016	37.33%	0.0076	-0.0711	55.18%	0.0071	-0.1263
80.0	52.87%	0.0059	0.083465	44.03%	0.0067	-0.0054	61.86%	0.0067	-0.0943
90.0	58.73%	0.0051	0.175309	50.23%	0.0059	0.0605	67.39%	0.0062	-0.0542
100.0	63.86%	0.0045	0.259109	55.91%	0.0051	0.1257	71.98%	0.0057	-0.0078
110.0	68.35%	0.0039	0.335769	60.90%	0.0045	0.1892	75.80%	0.0051	0.0426
120.0	72.29%	0.0034	0.403849	65.75%	0.0039	0.2504	79.02%	0.0047	0.0970
130.0	75.74%	0.0030	0.464644	69.76%	0.0034	0.3090	81.72%	0.0042	0.1534
140.0	78.76%	0.0026	0.518564	73.71%	0.0030	0.3647	84.01%	0.0037	0.2108
150.0	81.40%	0.0023	0.566346	76.86%	0.0026	0.4172	85.95%	0.0033	0.2680
160.0	83.72%	0.0020	0.608529	80.02%	0.0023	0.4665	87.62%	0.0030	0.3245
170.0	85.75%	0.0018	0.64578	82.46%	0.0020	0.5126	89.03%	0.0026	0.3794
180.0	87.52%	0.0016	0.67869	84.96%	0.0018	0.5555	90.28%	0.0023	0.4323
190.0	89.08%	0.0014	0.70777	86.82%	0.0016	0.5953	91.34%	0.0020	0.4828
200.0	90.44%	0.0012	0.733585	88.76%	0.0014	0.6320	92.28%	0.0018	0.5305
210.0	91.63%	0.0010	0.756474	90.17%	0.0012	0.6660	93.09%	0.0016	0.5754
220.0	92.68%	0.0009	0.779028	91.54%	0.0010	0.6971	93.82%	0.0014	0.6153
230.0	93.59%	0.0008	0.797323	92.72%	0.0009	0.7258	94.46%	0.0012	0.6542
240.0	94.39%	0.0007	0.813762	93.76%	0.0008	0.7519	95.03%	0.0010	0.6901
250.0	95.09%	0.0006	0.828596	94.65%	0.0007	0.7759	95.53%	0.0009	0.7232
260.0	95.70%	0.0005	0.842051	95.42%	0.0006	0.7977	95.99%	0.0008	0.7533
270.0	96.24%	0.0005	0.854306	96.09%	0.0005	0.8176	96.39%	0.0007	0.7808
280.0	96.71%	0.0004	0.865514	96.66%	0.0005	0.8356	96.76%	0.0006	0.8058
290.0	97.12%	0.0004	0.875804	97.16%	0.0004	0.8520	97.09%	0.0005	0.8283
300.0	97.48%	0.0003	0.885282	97.58%	0.0004	0.8669	97.38%	0.0004	0.8485
310.0	97.80%	0.0003	0.894036	97.95%	0.0003	0.8804	97.65%	0.0004	0.8667
320.0	98.07%	0.0002	0.902144	98.26%	0.0003	0.8926	97.89%	0.0003	0.8830
330.0	98.31%	0.0002	0.909668	98.52%	0.0002	0.9036	98.10%	0.0003	0.8975
340.0	98.52%	0.0002	0.916658	98.75%	0.0002	0.9135	98.30%	0.0002	0.9103
350.0	98.71%	0.0002	0.923159	98.94%	0.0002	0.9225	98.47%	0.0002	0.9218
360.0	98.87%	0.0001	0.92921	99.11%	0.0002	0.9305	98.63%	0.0002	0.9319
370.0	99.01%	0.0001	0.934842	99.25%	0.0001	0.9378	98.77%	0.0001	0.9408
380.0	99.13%	0.0001	0.940083	99.37%	0.0001	0.9443	98.90%	0.0001	0.9486
390.0	99.24%	0.0001	0.944959	99.47%	0.0001	0.9502	99.02%	0.0001	0.9555
400.0	99.34%	0.0124	0.949492	99.55%	0.0001	0.9555	99.12%	0.0001	0.9615

The graph of predicted and actual feed TBP curves for pure BNC and TNC is shown in Figure 4.4.4(a) and (b) respectively.

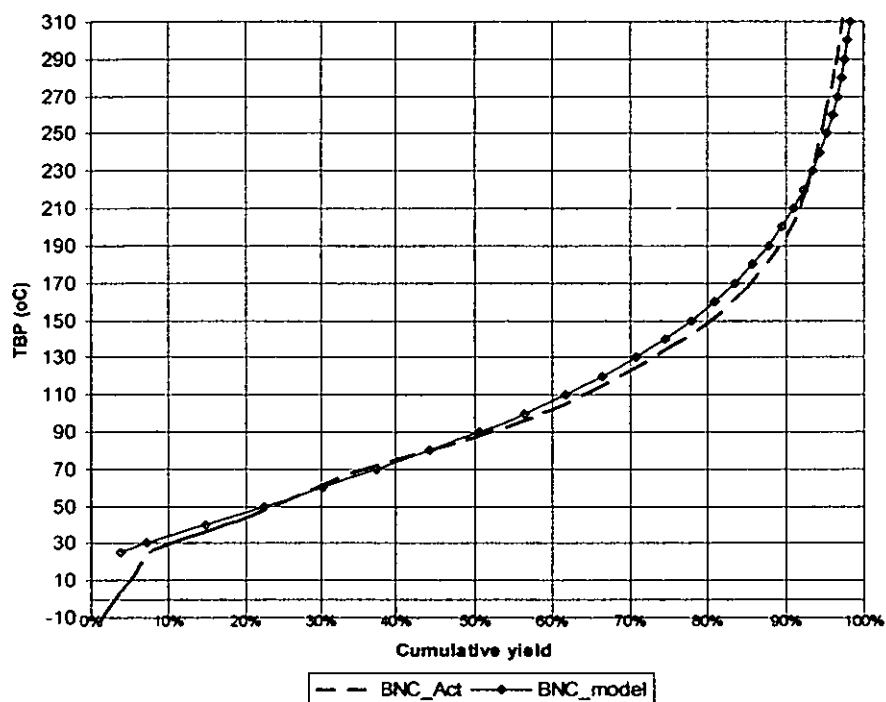


Figure 4.4.4(a) Predicted and actual Feed TBP curves for pure BNC

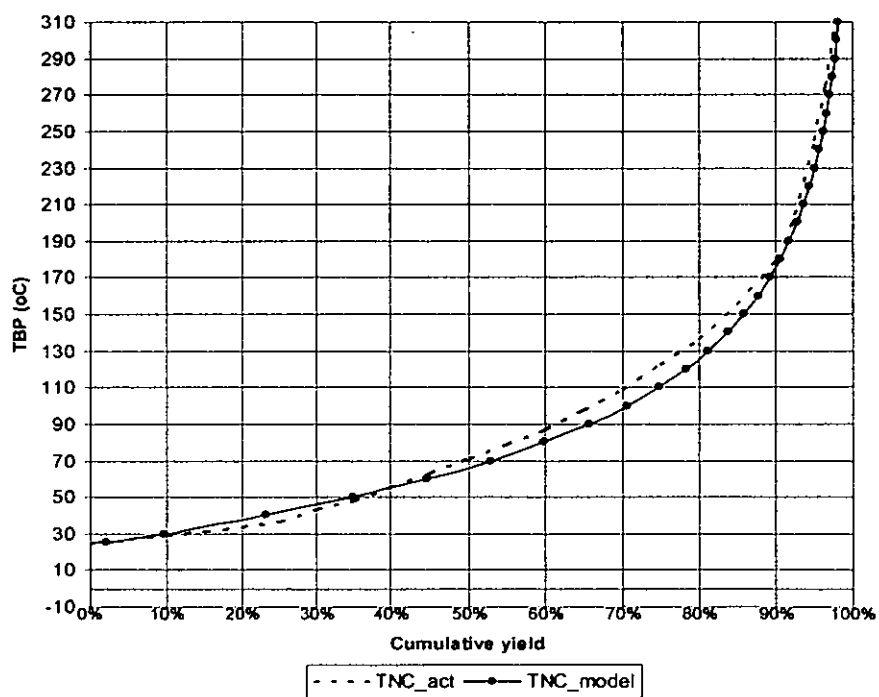


Figure 4.4.4(b) Predicted and actual Feed TBP curves for pure TNC

The %D and %AAD were calculated against actual TBP. The summary of %D and %AAD for pure BNC and TNC are tabulated in table 4.4.4(a) and (b) respectively.

Table 4.4.4(a) %D and %AAD of predicted BNC TBP curve

cum vol %	TBP _{Assays} (°C)	TBP _{model} (°C)	[% D]
10.00%	29.83	33.81	13.34%
30.00%	60.96	59.81	1.88%
50.00%	86.67	89.04	2.73%
70.00%	123.00	128.35	4.35%
90.00%	194.31	203.11	4.53%
95.00%	257.85	246.34	4.46%
		%AAD	5.22%

Table 4.4.4(b) %D and %AAD of predicted TNC TBP curve

Cumulative yield (vol %)	TBP _{Assays} (°C)	TBP _{model} (°C)	[% D]
10.00%	29.06	29.91	2.92%
30.00%	43.44	45.37	4.44%
50.00%	71.02	66.69	6.10%
70.00%	108.94	99.75	8.44%
90.00%	179.07	172.36	3.75%
95.00%	244.79	218.86	10.59%
		%AAD	6.04%

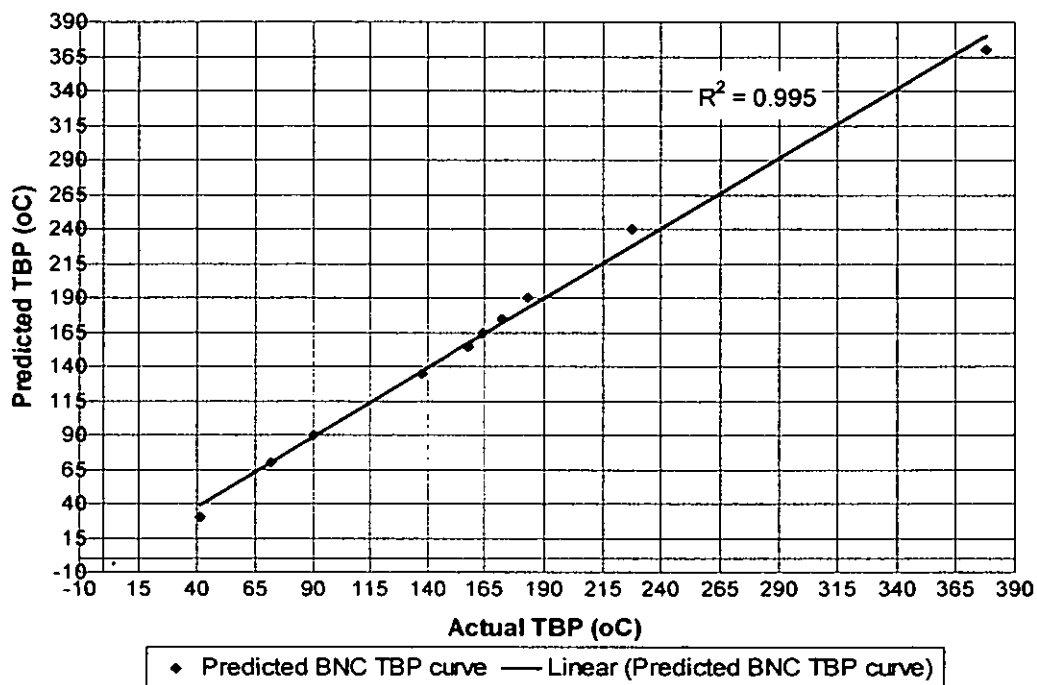


Figure 4.4.5(a) Comparison of predicted TBP curve with experimental data for pure BNC

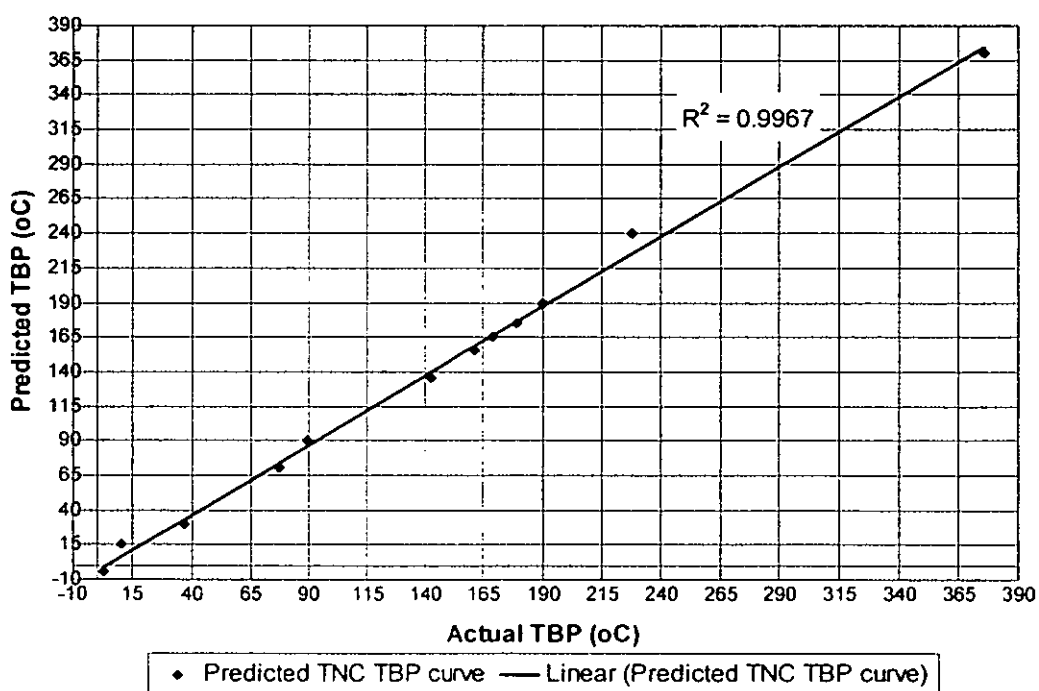


Figure 4.4.5(b) Comparison of predicted TBP curve with experimental data for pure TNC

The results showed that %AAD and R^2 for pure BNC and TNC is 5.224% and 0.995 and is 6.04% and 0.997 respectively. These are sufficiently good. In actual fact, the desired product for Condensate Tower is Heavy Naphtha. Based on the Condensate Tower operation trending, the boiling range is 70°C to 170°C. Boiling ranges of typical crude oil fractions is given in Table 1 of chapter 1. From the actual TBP curves, the boiling range falls between cumulative yield 35% to 85% for BNC and 50% to 90% respectively. If %AAD is calculated based on these cumulative yield ranges i.e. for pure BNC, the cumulative yield from 30% to 90% and for TNC, from 10% to 90%, the %AAD for BNC and TNC is reduced to 3.59% and 5.13% respectively.

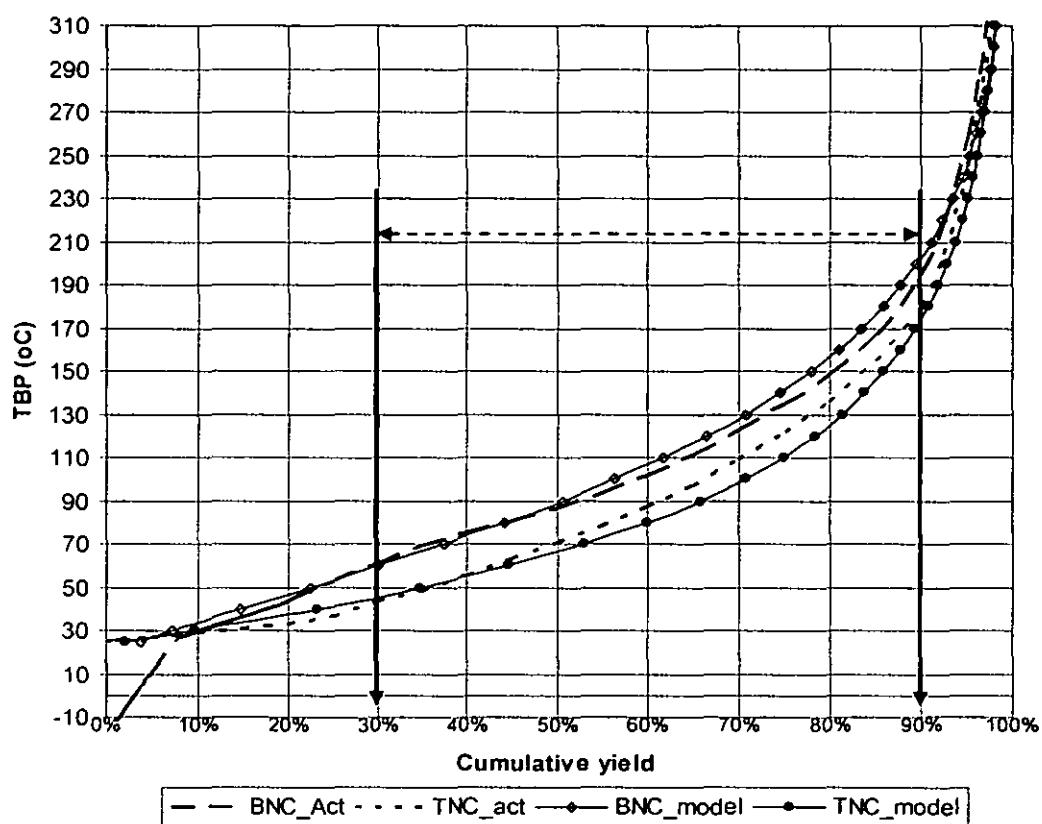


Figure 4.4.6 Predicted TBP curve with experimental data for pure BNC and TNC at desired distillate product boiling range

4.6.3 Prediction SG distribution in pure condensates using Hybrid GDM-PcLE method

A summary of distillate product SG used to predict SG distribution in blended condensates are summarised in table 4.4.5a and 4.4.5b.

Table 4.4.5a SG of Distillate product at $\alpha = 0.5$

Distillate products	cum vol %	Average cumulative (%)	SG _{Feed}
Top prod	48.73%	24.19%	0.648
Naphtha	33.63%	65.18%	0.754
Bottom prod	18.00%	91.00%	0.818

Table 4.4.5b SG of Distillate product at $\alpha = 1$

Distillate products	cum vol %	Average cumulative (%)	SG _{Feed}
Top prod	41.82%	20.91%	0.660
Naphtha	35.10%	59.37%	0.760
Bottom prod	23.08%	88.46%	0.817

SG distribution in blended condensate is developed using GDM, and the results are shown in figure 4.4.7a and figure 4.7.4b.

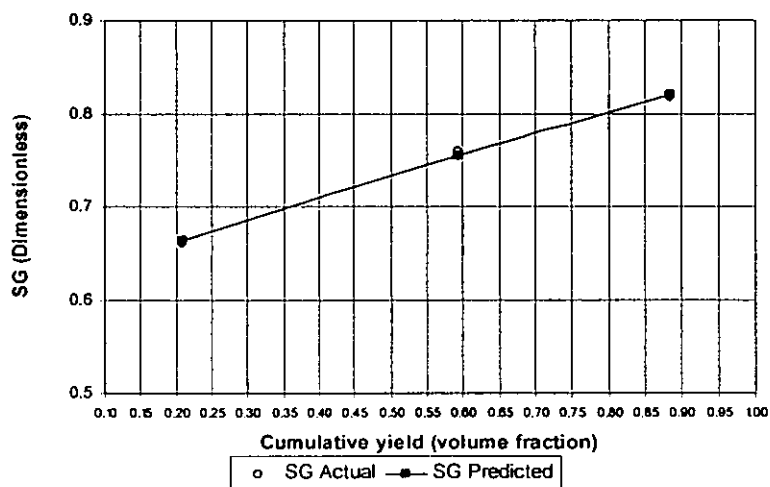


Figure 4.4.7a SG distribution in blended feed at $\alpha = 0.5$

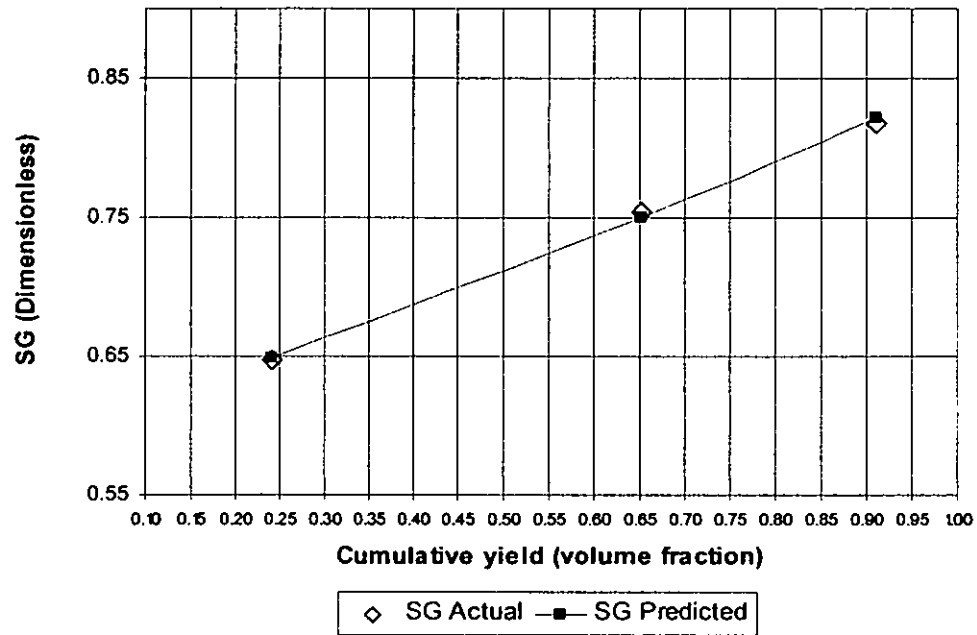


Figure 4.4.7b SG distribution in blended feed at $\alpha = 1$

By using the same pseudo-components as defined in section 4.4.3 above, SG at cumulative average volume fraction were determined. The SG calculation is shown in Appendix 5.

The gradient m and constant c of linear equation for each pseudo-component at $\alpha = 0.5$ and $\alpha = 1$ were calculated. Pure TNC is where $\alpha = 0$. Therefore the slope m and intersect c of each linear pseudo component equations at $\alpha = 0$ is determined using Gauss method. The results are shown in table 4.4.6.

Table 4.4.6 The slope m and intersect c of each SG's PcLE at various α

At $\alpha = 0.5$				At $\alpha = 1$				At $\alpha = 0$	
X_{ave}	SG	m	c	X_{ave}	sg	m	c	m	c
0.39%	0.421			1.23%	0.505				
1.84%	0.491	4.8034	0.4024	3.09%	0.549	2.3839	0.4758	4.803393	0.402356
5.65%	0.551	1.5843	0.4617	5.46%	0.580	1.2720	0.5101	1.584347	0.461693
13.69%	0.607	0.6962	0.5119	10.96%	0.620	0.7364	0.5393	0.696165	0.511882
23.83%	0.648	0.4024	0.5521	18.63%	0.654	0.4488	0.5709	0.402388	0.552094
33.04%	0.675	0.2975	0.5771	26.33%	0.679	0.3233	0.5942	0.297532	0.577084
41.29%	0.696	0.2535	0.5916	33.78%	0.699	0.2642	0.6098	0.253471	0.591643
48.62%	0.713	0.2321	0.6005	40.84%	0.715	0.2321	0.6207	0.232132	0.600454
55.11%	0.728	0.2222	0.6053	47.42%	0.730	0.2139	0.6281	0.222243	0.605262
60.84%	0.740	0.2193	0.6069	53.48%	0.742	0.2041	0.6327	0.219301	0.606884
65.87%	0.751	0.2212	0.6057	59.02%	0.753	0.1999	0.6350	0.221206	0.605725
70.29%	0.761	0.2269	0.6020	64.03%	0.763	0.2000	0.6350	0.226895	0.601977
74.16%	0.771	0.2358	0.5957	68.54%	0.772	0.2034	0.6328	0.235828	0.595698
77.54%	0.779	0.2478	0.5869	72.57%	0.781	0.2098	0.6284	0.247756	0.586852
80.50%	0.787	0.2626	0.5753	76.16%	0.788	0.2191	0.6216	0.262612	0.575333
83.08%	0.794	0.2805	0.5610	79.33%	0.796	0.2312	0.6124	0.280455	0.560969
85.33%	0.801	0.3014	0.5435	82.14%	0.803	0.2462	0.6005	0.301444	0.543535
87.29%	0.807	0.3258	0.5227	84.60%	0.809	0.2643	0.5856	0.325805	0.522744
88.99%	0.813	0.3539	0.4983	86.75%	0.815	0.2858	0.5674	0.353862	0.498254
90.47%	0.819	0.3860	0.4697	88.63%	0.821	0.3112	0.5454	0.385998	0.469657
91.75%	0.824	0.4227	0.4365	90.26%	0.827	0.3408	0.5191	0.422678	0.436473
92.87%	0.829	0.4644	0.3981	91.68%	0.832	0.3754	0.4879	0.464447	0.398148
93.84%	0.834	0.5119	0.3540	92.91%	0.837	0.4156	0.4511	0.511941	0.354041
94.68%	0.839	0.5659	0.3034	93.96%	0.842	0.4623	0.4077	0.565896	0.303411
95.40%	0.844	0.6272	0.2454	94.87%	0.847	0.5164	0.3568	0.627164	0.245405
96.03%	0.848	0.6967	0.1790	95.65%	0.851	0.5794	0.2971	0.696724	0.179043
96.58%	0.852	0.7757	0.1032	96.32%	0.856	0.6525	0.2271	0.7757	0.103201
97.05%	0.856	0.8654	0.0166	96.89%	0.860	0.7376	0.1452	0.865387	0.016585
97.45%	0.860	0.9673	-0.0823	97.38%	0.864	0.8366	0.0493	0.967267	-0.08229
97.80%	0.864	1.0830	-0.1951	97.79%	0.868	0.9521	-0.0632	1.08304	-0.19511
98.11%	0.868	1.2147	-0.3238	98.14%	0.872	1.0868	-0.1949	1.214664	-0.32384
98.37%	0.871	1.3644	-0.4707	98.44%	0.875	1.2443	-0.3495	1.364385	-0.47073
98.60%	0.875	1.5348	-0.6383	98.69%	0.879	1.4287	-0.5311	1.534777	-0.63835
98.79%	0.878	1.7288	-0.8297	98.91%	0.883	1.6449	-0.7444	1.7288	-0.82965
98.96%	0.882	1.9499	-1.0480	99.09%	0.886	1.8987	-0.9954	1.949858	-1.04804
99.11%	0.885	2.2019	-1.2974	99.24%	0.889	2.1971	-1.2911	2.201855	-1.29742
99.23%	0.888	2.4893	-1.5823	99.36%	0.892	2.5485	-1.6398	2.489279	-1.58227
99.34%	0.891	2.8173	-1.9078	99.47%	0.896	2.9629	-2.0516	2.817297	-1.90777

Predicted SG distribution in TNC was reconstructed using the calculated m and c at $\alpha = 0$. Figure 4.4.8(a) and (b) below shows the comparison between the predicted SG against SG extracted from the condensate assays for both pure BNC and TNC respectively.

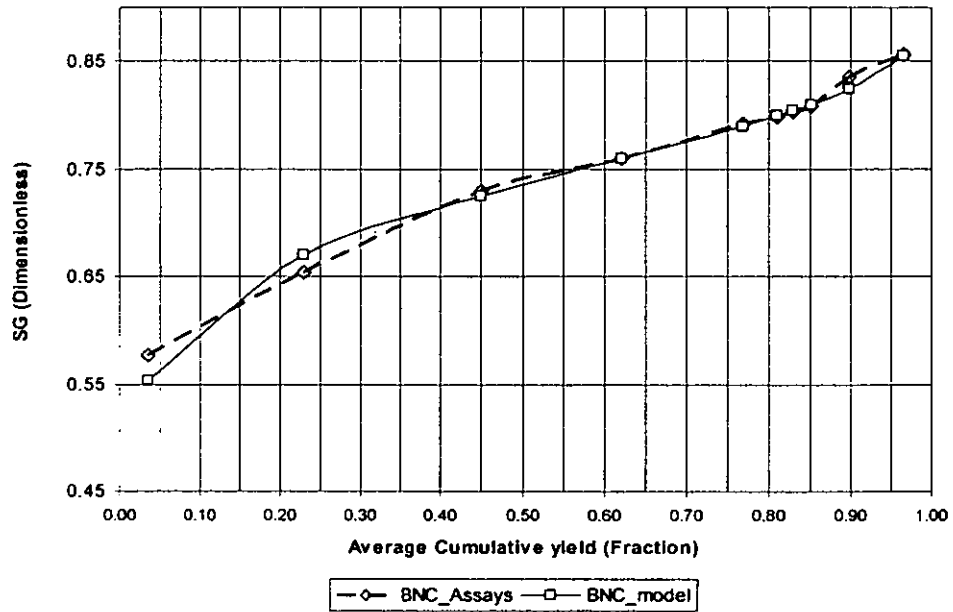


Figure 4.4.8(a) Predicted and actual SG distribution in pure BNC

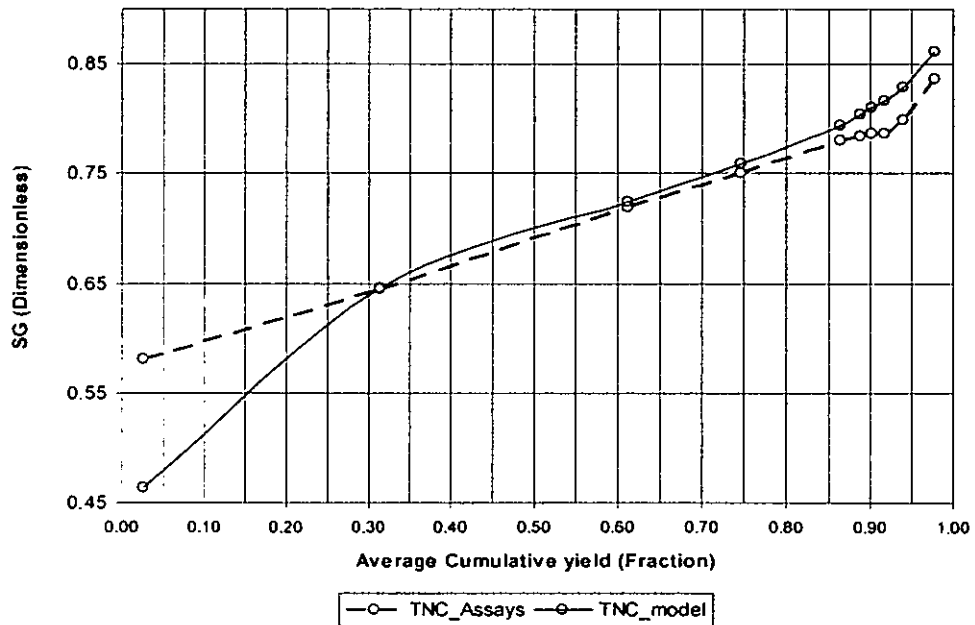


Figure 4.4.8(b) Predicted and actual SG distribution in pure TNC

From the graph, it is showed that largest deviation occurs at the fist cut i.e. the most volatile fraction. This is mainly due to small number of input points used i.e. only

three points. The %D and %AAD of predicted SG against condensate assays data were calculated and summarised in Table 4.4.7(a) and (b) below.

Table 4.4.7(a) %D and %AAD of predicted SG distribution in BNC

Average Cumulative Yield (%)	Condensate assays	Predicted value	% D
3.36%	0.58	0.55	3.92%
22.85%	0.65	0.67	2.54%
44.85%	0.73	0.73	0.62%
62.19%	0.76	0.76	0.05%
76.99%	0.79	0.79	0.17%
81.14%	0.80	0.80	0.21%
82.98%	0.80	0.80	0.10%
85.18%	0.81	0.81	0.29%
89.78%	0.84	0.82	1.44%
96.60%	0.86	0.85	0.23%
%AAD			0.96%

Table 4.4.7(b) %D and %AAD of predicted SG distribution in TNC

Average Cumulative Yield (%)	Condensate assays	Predicted value	% D
2.59%	0.58	0.51	11.40%
31.34%	0.64	0.67	4.32%
61.19%	0.72	0.74	2.83%
74.65%	0.75	0.77	2.58%
86.32%	0.78	0.80	2.63%
88.86%	0.78	0.81	3.18%
90.26%	0.79	0.81	3.48%
91.65%	0.79	0.82	4.14%
93.96%	0.80	0.83	3.88%
97.81%	0.84	0.86	2.62%
%AAD			4.11%

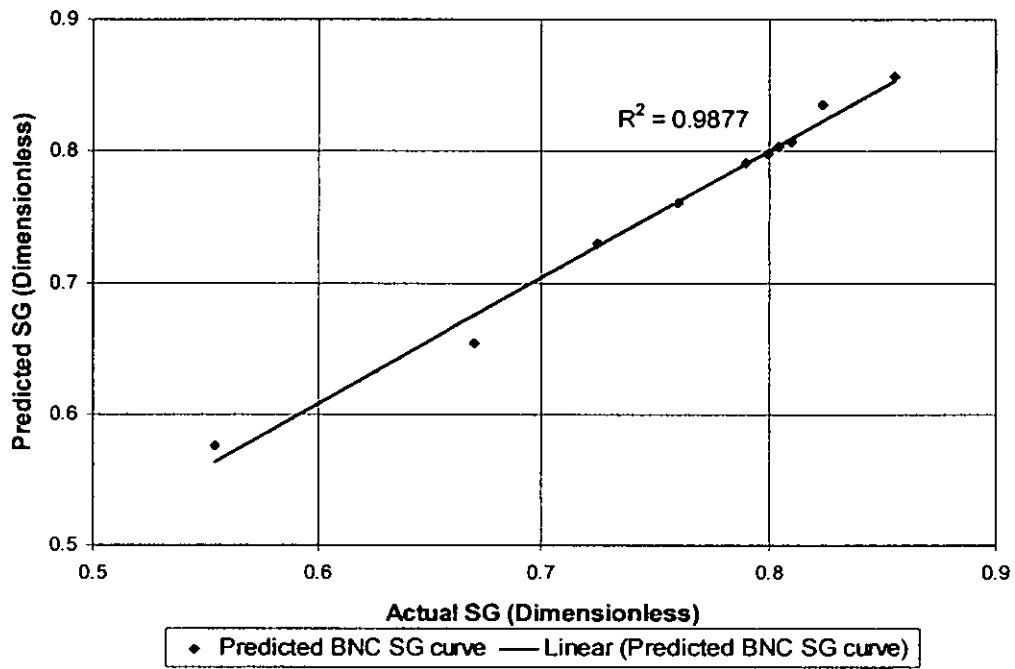


Figure 4.4.9(a) Comparison of predicted SG curve with experimental data for pure BNC

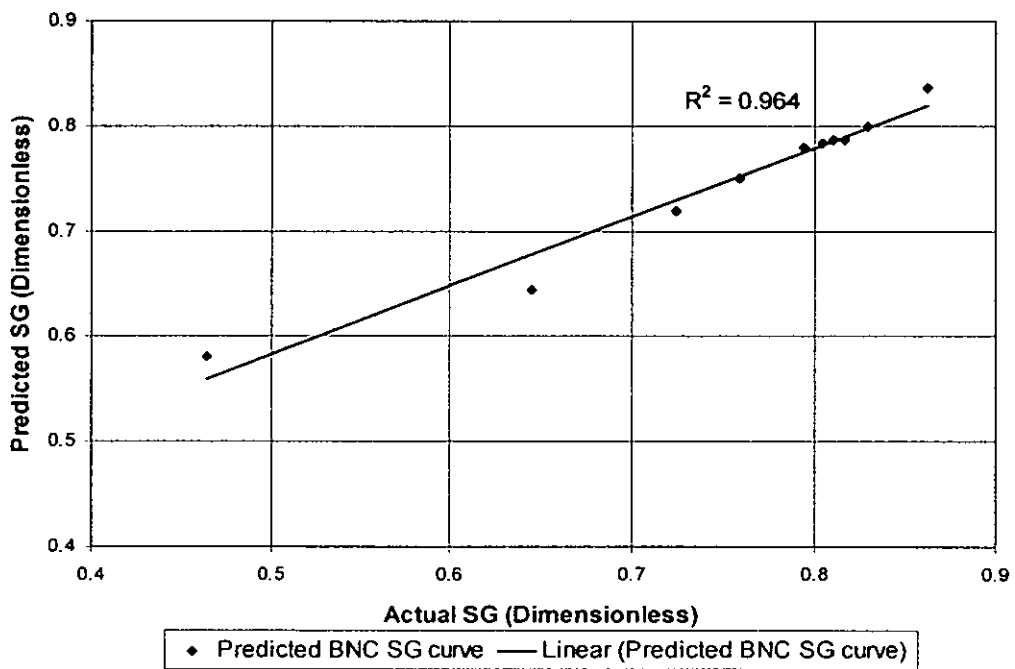


Figure 4.4.9(b) Comparison of predicted SG curve with experimental data for pure BNC

The results showed that %AAD and R2 for pure BNC and TNC is 0.96% and 4.11% and 0.987 and 0.964 respectively which are considerable good and acceptable with minimum number of data points used.

4.6.4 Optimisation of the desired product yields

The CFU has been designed to either feed with 100% BNC or 50:50 blending ratio of BNC and TNC, which is depends on TNC stock availability. Therefore in this case study, maximizing of the desired product yield is the objective function, where in this case is Naphtha.

The optimisation of Naphtha yield can be done using the predicted TBP curve of pure condensates. The cut points for various crude oil fractions as the Table 1.2 of chapter 1 was used as a reference. The proposed maximum swing cuts of Heavy Naphtha for BNC and TNC are + 10 °C and - 10 °C of the top and bottom cut points. Figure 4.5.1 (a) and (b) show the swing cuts for pure BNC and TNC respectively.

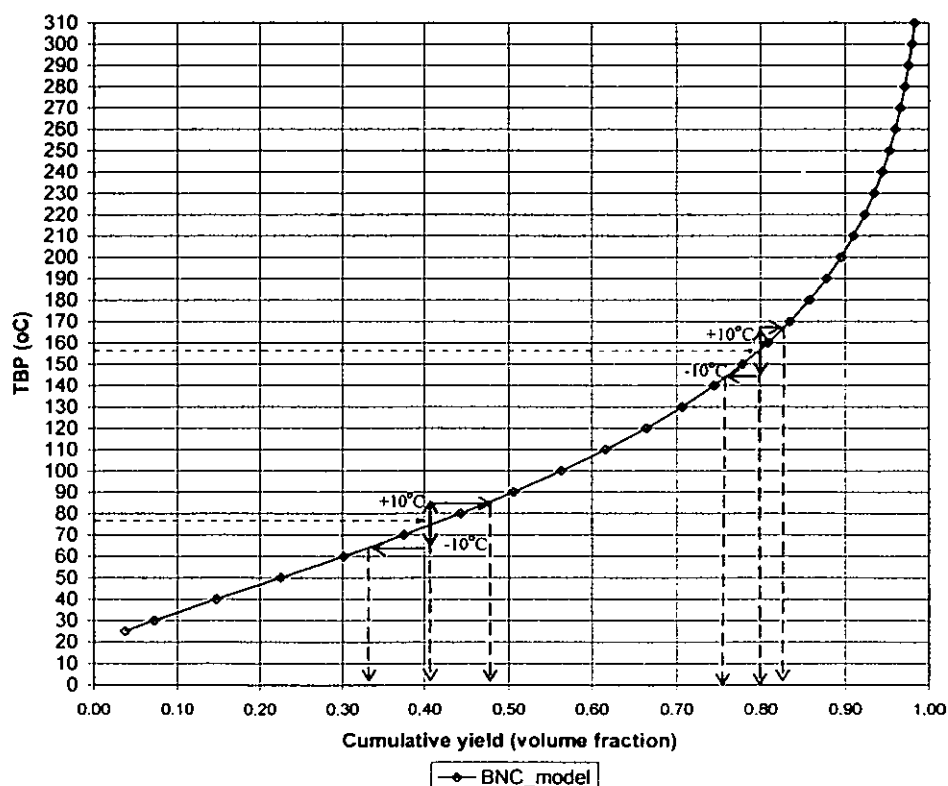


Figure 4.5.1(a) Swing cuts of Naphtha IP and EP for pure BNC

The summary of the potential yield for each distillate products are given in Table 4.5.1(a) to (d) for pure BNC and Table 4.5.2(a) to (d) below.

Table 4.5.1(a) Swing cut of Top product / Naphtha cut point for BNC

Top product				Naphtha			
TBP (EP) (°C)	cumulative yield	Yield	Gain	TBP (EP) (°C)	cumulative yield	Yield	Gain
85	47.50%	47.50%	6.60%	155	79.38%	31.88%	-6.60%
75	40.90%	40.90%	0.00%	155	79.38%	38.48%	0.00%
65	33.90%	33.90%	-7.00%	155	79.38%	45.48%	7.00%

Table 4.5.1(b) Swing cut of Naphtha / Bottom product cut point for BNC

Naphtha				Bottom product			
TBP (EP) (°C)	cumulative yield	Yield	Gain	TBP (EP) (°C)	cumulative yield	Yield	Gain
165	82.20%	41.30%	2.82%	380	100%	17.80%	-2.82%
155	79.38%	38.48%	0.00%	380	100%	20.62%	0.00%
145	76.20%	35.30%	-3.18%	380	100%	23.80%	3.18%

Table 4.5.1(c) Swing cut of Top product / Naphtha & Naphtha / Bottom product cut point for BNC

Top product				Naphtha				Bottom product			
TBP (EP) (°C)	Cum. yield	Yield	Gain	TBP (EP) (°C)	Cum. yield	Yield	Gain	TBP (EP) (°C)	Cum. yield	Yield	Gain
85	47.50	47.50	6.60	165	82.20	34.70	-3.78	380	100	17.80	-2.82
65	33.90	33.90	-7.00	145	76.20	42.30	3.82	380	100	23.80	3.18
85	47.50	47.50	6.60	145	76.20	28.70	-9.78	380	100	23.80	3.18
65	33.90	33.90	-7.00	165	82.20	48.30	9.82	380	100	17.80	-2.82

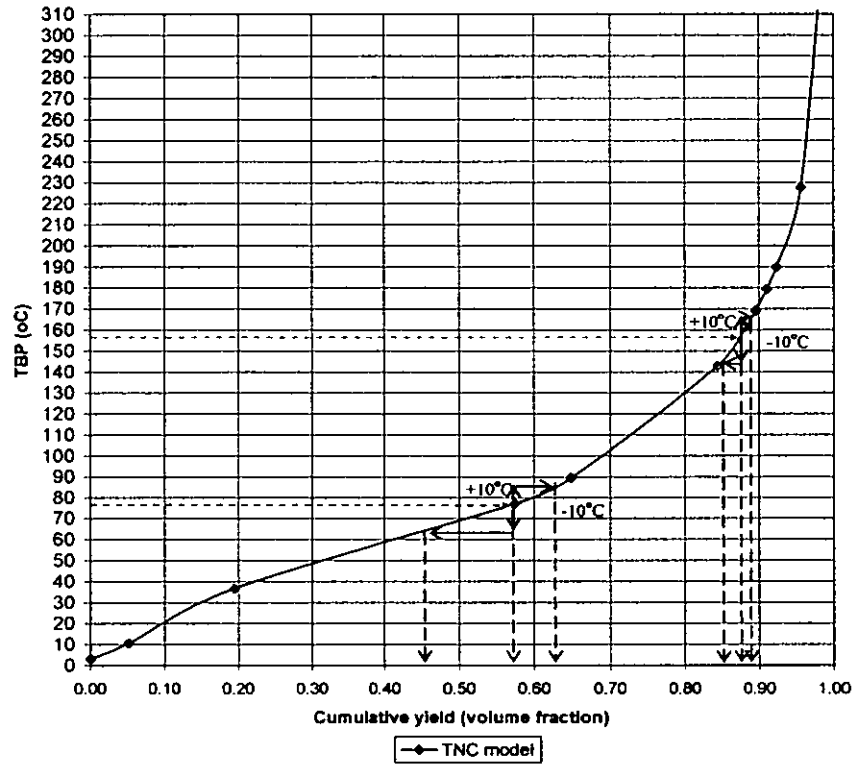


Figure 4.5.1(b) Swing cuts of Naptha IP and EP for pure TNC

Table 4.5.2(a) Swing cut of Top product / Naptha cut point for TNC

Top product				Naptha			
TBP (EP) (°C)	Cum. yield	Yield	Gain	TBP (EP) (°C)	Cum. yield	Yield	Gain
85	62.37%	62.37%	6.30%	155	87.02%	24.66%	-6.30%
75	56.07%	56.07%	0.00%	155	87.02%	30.96%	0.00%
65	48.66%	48.66%	-7.41%	155	87.02%	38.36%	7.41%

Table 4.5.2(b) Swing cut of Naptha / Bottom product cut point for TNC

Naptha				Bottom product			
TBP (EP) (°C)	Cum. yield	Yield	Gain	TBP (EP) (°C)	Cum. yield	Yield	Gain
165	88.83%	26.47%	1.81%	380	100.00%	11.17%	-1.81%
155	87.02%	24.66%	0.00%	380	100.00%	12.98%	0.00%
145	84.91%	22.55%	-2.11%	380	100.00%	15.09%	2.11%

Table 4.5.2(c) Swing cut of Top/Naptha & Naptha/Bottom cut points for TNC

Top product				Naphtha				Bottom product			
TBP (EP) (°C)	Cum. yield	Yield	Gain	TBP (EP) (°C)	Cum. yield	Yield	Gain	TBP (EP) (°C)	Cum. yield	Yield	Gain
85	62.37%	62.37%	6.30%	165	88.83%	26.47%	-4.49%	380	100%	11.17%	-3.92%
65	48.66%	48.66%	-7.41%	145	84.91%	36.25%	5.30%	380	100%	15.09%	0.00%
85	62.37%	62.37%	6.30%	145	84.91%	22.55%	-8.41%	380	100%	15.09%	0.00%
65	48.66%	48.66%	-7.41%	165	88.83%	40.17%	9.22%	380	100%	11.17%	-3.92%

For a case study on process optimisation, assumed that the refinery decided to maximise the Naphtha yield, however at the same time to maintain the top product yield around 45%. By using the “solver” application of Excel, the maximum Naphtha yield is achieved at $\alpha = 0.70$ with the yield of 33% and Bottom product yield is about 18% as shown in Figure 4.5.2 below.

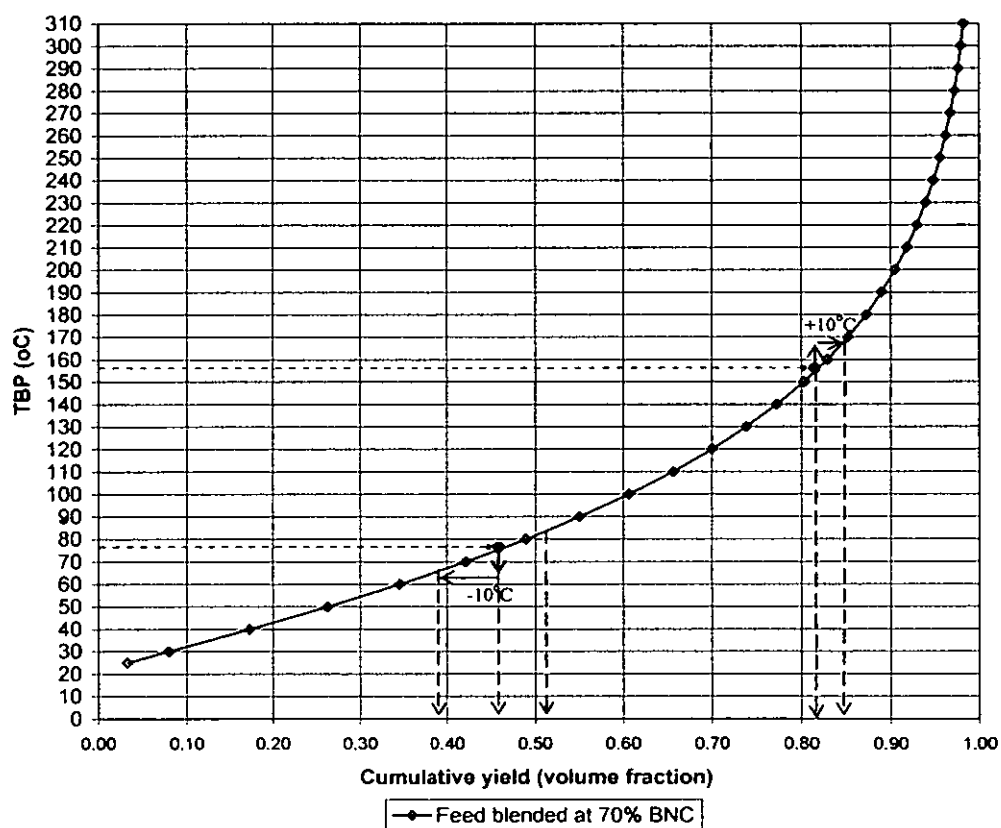


Figure 4.5.2 Blended feed TBP curve at $\alpha = 0.7$ with swing cuts of Naphtha IP and EP

To further enhance the recovery by adopting swing cuts method, only increasing the cut point of Naphtha / bottom to 165 °C is feasible to gain another 5% naphtha yield. However, the Top product / Naphtha cut point can be reduced below 65°C because this will reduce the top product yield < 45%. Thus, knowing each pure condensate TBP curve and adopting swing cut method could assist refinery plant operation engineer to explore and exploit the columns (Condensate Tower and Condensate Stabiliser) operating flexibility that meets overall refinery demand.

Therefore the above information are very useful for refinery to maximise the desired product yield using simple LP like “solver” and determine the optimum operating conditions by exploring and exploiting the columns (Condensate Tower and Condensate Stabiliser) operating flexibility to meet overall refinery demand.

CHAPTER V

CONCLUSIONS AND FUTURE WORKS

5.1 Conclusions

The results of the proposed methodology and a case study in chapter IV were used to conclude the findings, as deliberated in the following sections of this chapter.

5.2 Existing models used to predict TBP, SG and K_{vis} distribution in blended Condensates

The results of the existing model used to predict blended feed distillation curves for TBP, SG and K_{vis} showed that GDM can predict sufficiently good for TBP curve and SG distribution, but not for K_{vis} . Even though the NCM gave better accuracy of predicting the SG and K_{vis} distribution in blended feed compared to GDM, the “helical characteristic” of the predicted distillation curve demonstrated by NCM and lengthy iteration required make this model less attractive to be used in this research methodology.

Therefore, GDM is found to be the most suitable model to be used in this study in term of accuracy, simplicity and faster ness.

5.3 Simplification of the Feed synthesis procedure and a Hybrid GDM-PcLE method

The results showed that the predicted blended condensate TBP curve and SG distribution using the proposed short cut feed synthesis procedure are almost agreeable with those measured in the laboratory. In fact the accuracy can be improved further if the distillates samples and measurements of feed and distillate products flow rates are to be carried out simultaneously and more precisely i.e. the distillate product

are sampled at the same time & date and flow meters are calibrated and the measurements are corrected to density & temperature of the measuring devices. A case study using the proposed short cut feed synthesis procedure and a hybrid GDM-PcLE model showed that the Naphtha yield can be increased by 5% by changing the current feed blending ratio and product cut points.

The proposed hybrid GDM-PcLE model is also useful for refinery planning and plant engineers because of its simplicity, where the inputs are extracted from readily available databank and need less time to arrive for the results compare to the one simulated using commercial software and expensive feed on line analysers. Definitely, this would give significant initiative improvement to refinery plant and operation engineers to explore the flexibility of the distillation column operating parameters to maximise the desired product yields.

5.4 Summary

The conclusion can be summarised as follows:

1. GDM is the most suitable model to be used in this study, compared to NCM in term of accuracy, simplicity and faster ness.
2. The proposed procedure simplifying the current practices by eliminating the iterative process as required the current practises of using Hysis 3.1TM or petrosimTM, yet predicting results are almost agreeable with those measured in the laboratory.
3. The accuracy can be improved further if the distillates samples and measurements of feed and distillate products flow rates are to be carried out simultaneously and more precisely i.e. the distillate product are sampled at the same time & date and flow meters are calibrated and the measurements are corrected to density & temperature of the measuring devices.

5.5 Future works

The proposed method and improvement of the current procedure developed in this work has been shown to provide good prediction of TBP and SG distillation curves in individual component of the blended condensate.

The proposed short cut procedure and Hybrid GDM-PcLE model can be extended to the blended crude oil that feed into wide range of distillate products of the Atmospheric Distillation column. Since PcLE method is simple and open application, it can be easily integrated with available commercial software to enhance its application predicting the pure component TBP and other distillation curves from blended feed.

As a summary, the followings are potential future works:

1. Extend the proposed short cut procedure predicting pure component TBP and distillation curves of crude oil from the blended crude oil that feed into widen distillate product range of the Atmospheric Distillation column
2. Integrate PcLE method with other model that could give better accuracy
3. Integrate with iCONTM, Petronas in-house process simulation software that is equivalent to Hysis. It is a great potential for PcLE method to be integrated in iCON's feed synthesis application to predict pure component TBP and other distillation curves of the blended crude oil

REFERENCES

- Dutt, N.V.K. (1990). A simple method of estimating the viscosity of petroleum crude oil and fractions. *The Chemical Engineering Journal*, 45, 83-86
- Doug Hyung Lee, Euy Soo Lee and Sang Jin Park. (2006). Characterization of crude feed and products from operating conditions by using continuous probability functions and inferential models. *Korean J. Chem. Eng.*, 23(4), 517-521
- Egon Eckert *, Tom´aš Vaněk. (2005). New approach to the characterization of petroleum mixtures used in the modeling of separation processes. *Computers and Chemical Engineering*, 30, 343-356
- Falla, (2006). Characterization of crude petroleum by NIR, *Journal of PSE*
- Gary, Handwerk and Kaiser, (2007) Refining processes
- Goossens A.G. (1996). Prediction of molecular weight of petroleum fractions, *Industrial and engineering chemistry research*, Volume 35, Issue 3, Pages 985-988
- Hsu and Robinson, (2006) Refining Processing Handbook, Elsevier
- James H. G. (2001). Petroleum Refining Technology and Economics, Marcel Dekker.
- James G. S. (2002). Petroleum Refining Process, Marcel Dekker,
- Jones D.S.J (1999). Elements of Petroleum Processing, Wiley.
- Juan G.P., Nan Z. (2008). Constantinos Theodoropoulos Characterisation of heavy petroleum fractions using modified molecular-type homologous series (MTHS) representation, *Energy* 33 p974-987
- Li, C., He, X., Chen, B., Chen, B., Gong, Z., Zhang, Q. (2005). Optimal TBP cut points in supply chain management of refinery enterprises, *Huagong Xuebao/Journal of Chemical Industry and Engineering (China)*, Volume 56, Issue 11, Pages 2142-2145
- Maples R.E. (1997). Linear regression determines crude properties at variable boiling points, *Oil and Gas Journal* Volume 95, Issue 44, Pages 72+
- Miquel J, Castells, F. (1994). Easy characterization of petroleum fractions, *Hydrocarbon processing*, Volume 73, Issue 1, Pages 99-103
- Motlaghi S., Jalali F., Ahmadabadi M.N. (2008). An expert system design for a crude oil distillation column with the neural networks model and the process

- optimization using genetic algorithm framework, *Expert Systems with Applications* 35 p1540–1545
- Macias-Hernandez, J.J.; Angelov, P.; Xiaowei Z. (2007). Soft sensor for predicting crude oil distillation side streams using evolving takagi-sugeno fuzzy models, *Systems, Man and Cybernetics*. ISIC. IEEE International Conference Page(s):3305 – 3310
- Park, H.-K. (2001). Comprehensive assay database brings value to CDU optimization, *Hydrocarbon Asia* Volume 11, Issue 8, Pages 25-32
- Parkash S (2003) Refining Processing Handbook, Elsevier.
- Peter B. and Thivanka D. (2007). Classification and characterisation of crude oils based on distillation properties, *Journal of Petroleum Science and Engineering* 57 p166–180
- Ramin B. Boozarjomehry B., Farzad Abdolahi A., Mohammad A., Moosavian A., (2005). Characterization of basic properties for pure substances and petroleum fractions by neural network, *Fluid Phase Equilibria* 231 188–196
- Riazi M.R (2005) Characterisation and properties of petroleum fraction, ASTM annual series.
- Riazi M.R., Daubert, T.E. (1980). Simplify Property Predictions, *Hydrocarbon Processing*, Volume 59, Issue 3, Pages 115-116
- Riazi M.R., Daubert, T.E. (1987). Improved characterization of wide boiling range undefined petroleum fractions, *Industrial and engineering chemistry research*, Volume 26, Issue 3, Pages 629-632
- Riazi M.R. (1997). A Continuous Model for C7+ Fraction Characterization of Petroleum Fluids, *Industrial and engineering chemistry research* Volume 36, Issue 10, Pages 4299-4307
- Riazi M.R., Al-Adwani H.A., Bishara A. (2004). The impact of characterization methods on properties of reservoir fluids and crude oils: options and restrictions, *Journal of Petroleum Science and Engineering*, 42, 195– 207
- Sergio S., Jorge A., and William C. M. (2007). Comparison of Probability Distribution Functions for Fitting Distillation Curves of Petroleum, *Energy & Fuels* 21, 2955-2963
- Tareq A.A. (2006) Enhanced method for predicting the properties of light petroleum fractions. *Fuel* Volume 85 Issues 5-6, 748-754
- Thirtha C., Saraf D.N. (2004). On line estimation of product properties for crude distillation units, *Journal of Process Control* Volume 14 Issue 1 61-77

Thomas J. Bruno. (2006), Improvements in the Measurement of Distillation Curves 1. A Composition-Explicit Approach, *Ind. Eng. Chem. Res.*, 45 (12), 4371-4380

Wenkai Li, Chi-Wai H., Karimi I.A. and Rajagopalan S. (2007). A novel CDU model for refinery planning, *Asia-Pac. J. Chem. Eng.* 2: 282-293

N. Zhang, X.X. Zhu. (2000). A novel modeling and decomposition strategy for overall refinery, *Computers and Chemical Engineering*, 24 1543- 1548

<http://www.aspentech.com/products/aspens-hysys.cfm> (July 2008)

<http://www.petro-sim.com/default.petrosim.asp?id=1> (December 2008)

http://www.petronas.com.my/internet/corp/centralrep2.nsf/Src/WebDoc*Crude+Oil+Assays/?Open (October 2008)

APPENDICES

Appendix 1	Inter-conversion of various Distillation Data
Appendix 2	Condensate Assays
Appendix 3	Predicted results of blended feed TBP curve
Appendix 4	Predicted results of blended feed SG and Kvis distribution curves
Appendix 5	Case Study Results

Appendix 1: Inter-conversion of various Distillation Data

Conversion ASTM 86 to TBP

(1) Riazi-Daubert method

$$TBP = a \times (ASTMD86)^b$$

Vol %	a	b	ASTM range °C
0	0.9177	1.0019	20 - 320
10	0.5564	1.09	35 - 305
30	0.7617	1.0425	50 - 315
50	0.9013	1.0176	55 - 320
70	0.8821	1.0226	65 - 330
90	0.9552	1.011	75 - 345
100	0.8177	1.0355	75 - 400

Conversion EFV to TBP

$$EFV = a \times (TBP + 273)^b \times (SG)^c - 273$$

table.3.3

vol%	a	b	c	ASTM range (°C)
0	2.9747	0.8466	0.4209	10 - 265
10	1.4459	0.9511	0.1287	60 - 320
30	0.8506	1.0315	0.0817	90 - 340
50	3.268	0.8274	0.6214	110 - 355
70	8.2873	0.6871	0.934	130 - 400
90	10.6266	0.6529	1.1025	160 - 520
100	7.9952	0.6949	1.0737	190 - 430

Conversion SD to TBP**Daubert's method**

$$V_i = C \times W_i^{D^b}$$

Where V_i = difference in TBP between two cut points (K or °C); W_i = Observed difference in SD temperature between two cut points (K or °C); C and D are constants varying for each cut points and given in table below.

cut point range		C	D	max allowable , °C
100 - 95	V_1	0.03849	1.9733	15
95 - 90	V_2	0.90427	0.8723	20
90 - 70	V_3	0.37475	1.2938	40
70 - 50	V_4	0.25088	1.3975	40
50-30	V_5	0.0855	1.6988	40
30 - 10	V_6	0.02175	2.0253	40
10 - 0	V_7	0.20312	1.4296	20

Notes

$$\text{TBP (50 vol\%)} = \text{SD(50 wt\%)}$$

$$\text{TBP (5\%)} = \text{TBP(50\%)} - V_5 - V_6 - V_7$$

$$\text{TBP (10\%)} = \text{TBP(50\%)} - V_5 - V_6$$

$$\text{TBP (30\%)} = \text{TBP(50\%)} - V_5$$

$$\text{TBP (70\%)} = \text{TBP(50\%)} + V_4$$

$$\text{TBP (90\%)} = \text{TBP(50\%)} + V_4 + V_3$$

$$\text{TBP (95\%)} = \text{TBP(50\%)} + V_4 + V_3 + V_2$$

$$\text{TBP (100\%)} = \text{TBP(50\%)} + V_4 + V_3 + V_2 + V_1$$

Bintulu Condensate assay – summary

TRUE BOILING POINT DATA

CUT NUMBER	CUT POINT AET °C	METHOD USED	YIELD % ON CRUDE						DENSITY at 15 °C kg/l
			WEIGHT gram	WEIGHT %		VOLUME ml	VOLUME %		
				CUT	CUM		CUT	CUM	
1	LPO	ASTM D 2892	307.4	5.37	5.37	534.6	8.64	8.64	0.5750
2	70	ASTM D 2892	2154.2	37.65	43.02	3305.5	41.02	47.66	0.6517
3	90	ASTM D 2892	759.8	13.27	56.29	1029.1	12.77	60.42	0.7381
4	140	ASTM D 2892	1649.8	28.83	85.12	2150.1	26.67	87.09	0.7873
5	155	ASTM D 2892	203.9	3.60	88.72	258.3	3.21	90.31	0.7972
6	185	ASTM D 2892	288.6	5.01	93.73	354.5	4.41	94.72	0.8085
7	185+	ASTM D 2892	358.7	6.27	100.00	424.6	5.28	100.00	0.8447
WEIGHT OF SAMPLE (gm)			5722.2						
DENSITY @ 15°C OF CHARGE (kg/l)			0.7119						
VOLUME OF CHARGE @ 15°C (vol)			8037.9						

ANALYSIS FOR PRODUCT CUT

Tests	Method	Unit	RESULTS						
			C5 - 70	70 - 90	90 - 140	140 - 155	140 - 185	155 - 185	
Yield on Crude		vol %	41.02	12.77	26.67	3.21	7.62	4.41	
Yield on Crude		wt %	37.65	13.27	28.83	3.60	8.61	6.01	
Density @ 15 °C	ASTM D 4052	g/cm ³	0.6517	0.7381	0.7873	0.7972	0.8037	0.8085	
API Gravity	Calculated		NA	60.18	62.85	45.92	44.48	43.43	
Sulphur	ASTM D 3120	ppm wt	8	7	17	139			
Sulphur	ASTM D 4294	wt %					0.028	0.044	
Nitrogen	ASTM D 4829	ppm wt	<1	<1	<1	<1	<1	<1	
Total Acid Number	ASTM D 974	mgKOH/g				<0.05			
Smoke Point	ASTM D 1322	mm				17.0		18.6	
Flash Point (Abel)	IP 170	°C				29.8	35.0	41.0	
Flash Point (PMCC)	ASTM D 93	°C							
Freezing Point	ASTM D 2386	°C				<-75.0	<-75.0	<-75.0	
Aniline Point	ASTM D 811	°C				36.6	39.2	41.0	
Colour Saybolt	ASTM D 156	-	+30	+30	+30	+30	+30	+30	
Colour ASTM	ASTM D 1500	-							
Research Octane Number	ASTM D 2899	-							
Kinematic Viscosity @ - 20°C	ASTM D 445	cSt				1.722	2.000	3.494	
R Reid Vapour Pressure	ASTM D 5191	kPa	99.9	28.0	9.7				
Cetane Index	ASTM D 978	-				16.9		29.0	
Ash Content	ASTM D 482	wt %				<0.01	<0.01	<0.01	
Mercaptan Sulphur	IP 104	ppm wt					6	10	
Paraffins	DHA	vol %	89.88	34.17	37.13	49.89	48.89	41.99	
Olefins	DHA	vol %	0.00	0.00	0.00	0.00	0.00	0.00	
Naphthenes	DHA	vol %	8.86	61.70	44.86	19.67	18.72	19.23	
Aromatics	DHA	vol %	1.46	4.13	17.88	28.40	31.82	36.17	
Aromatics	DHA	vol %	0.00	0.00	0.18	2.04	2.68	3.81	
Naphthalene Content	ASTM D 1840	vol %				<0.1	<0.1	<0.1	
Mercury	CVAFS	ppb wt	< 1.0	< 1.0	< 1.0	2.76	2.70	2.16	
Distillation	ASTM D 86								
Initial Boiling Point		°C	35.5	73.5	100.0	142.5	@	155.0	
5%		°C	39.0	75.5	103.0	144.5		163.0	
10%		°C	40.0	76.0	103.5	145.0		164.0	
20%		°C	40.5	77.0	105.0	145.5		165.0	
30%		°C	41.0	78.0	106.0	146.0		166.0	
40%		°C	42.0	78.5	107.0	147.0		166.5	
50%		°C	43.5	79.0	109.0	147.5		167.5	
60%		°C	45.0	80.0	111.0	148.0		168.5	
70%		°C	45.0	81.0	114.0	149.0		170.0	
80%		°C	53.0	82.5	118.0	150.5		172.0	
90%		°C	60.0	85.0	125.0	153.0		175.0	
95%		°C	65.5	86.0	130.0	155.5		179.0	
Final Boiling Point		°C	76.5	91.0	137.0	159.0		189.0	
Recovery		vol %	95.0	98.5	98.5	98.5		98.5	
Residue		vol %	0.5	1.0	1.3	1.3		1.3	
Loss		vol %	1.5	0.5	0.2	0.2		0.2	

Remark :

- 1) @ - Insufficient sample to do the test
2) NA - Not applicable

Tests	Method	Unit	RESULT
Yield on Crude		vol %	5.28
Yield on Crude		wt %	6.27
Density @ 15 °C	ASTM D 4052	g/cm ³	0.8447
API Gravity	Calculated		35.93
Sulphur	ASTM D 4294	wt %	0.144
Flash Point (PMCC)	ASTM D 93	°C	74
Pour Point	ASTM D 97	°C	<-69.0
Total Acid Number	ASTM D 664	mgKOH/g	0.11
Nitrogen	ASTM D 4829	ppm wt	64
Ash Content	ASTM D 482	wt %	<0.01
MCRT - 100% Sample	ASTM D 4530	wt %	<0.01

Appendix 3: Predicted results of blended feed TBP curve

100% BNC

Calculations					Comparison Errors			
no.	vol.frac	cum vol.	Y	X	Exp. data	Predicted TBP	D%	[D%]
0	0.00%	0.00%			268.0	270.0	0.75%	0.75%
1	6.73%	6.73%	-2.708	-2.664	288.0	288.1	0.03%	0.03%
2	32.24%	38.97%	-1.308	-0.706	343.0	341.3	-0.50%	0.50%
3	11.75%	50.72%	-1.066	-0.346	363.0	361.7	-0.36%	0.36%
4	22.94%	73.66%	-0.671	0.288	408.0	412.9	1.20%	1.20%
5	6.66%	80.32%	-0.536	0.486	428.0	434.1	1.42%	1.42%
6	1.64%	81.96%	-0.474	0.538	438.0	440.2	0.50%	0.50%
7	2.04%	84.00%	-0.417	0.606	448.0	448.4	0.10%	0.10%
8	2.35%	86.35%	-0.336	0.689	463.0	459.1	-0.84%	0.84%
9	6.85%	93.20%	-0.105	0.989	513.0	503.3	-1.88%	1.88%
10	6.80%	99.50%	0.323	1.667	643.0	645.2	0.33%	0.33%
TBP ₀ (guess) 270			R ² = 0.9991		Average Absolute Deviation 0.717%			
A = 0.431		B = 1.429						

Blended TBP curve – 75% BNC and 25% TNC

cum. vol	TBP _{Experiment} , K	TBP _{GDM} , K	D%	[D%]
6.34%	288.00	288.14	0.049%	0.05%
43.61%	343.00	342.12	-0.257%	0.26%
54.26%	363.00	360.34	-0.732%	0.73%
76.35%	408.00	412.03	0.987%	0.99%
82.30%	428.00	432.94	1.154%	1.15%
83.85%	438.00	439.42	0.323%	0.32%
85.75%	448.00	448.12	0.026%	0.03%
87.84%	463.00	458.96	-0.873%	0.87%
93.80%	513.00	503.31	-1.889%	1.89%
100.00%	643.00	652.14	1.422%	1.42%
			AAD %	0.77%

Blended TBP curve – 50% BNC and 50% TNC

cum. vol	TBP _{Experiment} , K	TBP _{GDM} , K	D%	[D%]
5.95%	288.00	287.98	-0.006%	0.01%
48.24%	343.00	343.97	0.283%	0.28%
57.80%	363.00	360.37	-0.726%	0.73%
79.04%	408.00	412.51	1.105%	1.11%
84.27%	428.00	432.65	1.086%	1.09%
85.74%	438.00	439.41	0.322%	0.32%
87.50%	448.00	448.42	0.094%	0.09%
89.33%	463.00	459.07	-0.848%	0.85%
94.41%	513.00	501.49	-2.243%	2.24%
100.00%	643.00	648.46	0.849%	0.85%
			AAD %	0.76%

Blended TBP curve – 25% BNC and 75% TNC

cum. vol	TBP _{Experiment} , K	TBP _{GDM} , K	D%	D%
5.56%	288.00	288.00	0.001%	0.00%
52.88%	343.00	344.33	0.389%	0.39%
61.33%	363.00	359.05	-1.087%	1.09%
81.73%	408.00	412.68	1.148%	1.15%
86.24%	428.00	432.33	1.011%	1.01%
87.62%	438.00	439.61	0.368%	0.37%
89.25%	448.00	449.23	0.275%	0.28%
90.81%	463.00	459.90	-0.670%	0.67%
95.01%	513.00	500.73	-2.391%	2.39%
100.00%	643.00	648.95	0.926%	0.93%
AAD %				0.83%

Blended TBP curve – 100% TNC

cum. vol	TBP _{Experiment} , K	TBP _{GDM} , K	D%	D%
5.17%	288.00	288.00	0.000%	0.00%
57.51%	343.00	344.65	0.482%	0.48%
64.87%	363.00	357.81	-1.430%	1.43%
84.42%	408.00	413.52	1.354%	1.35%
88.21%	428.00	432.49	1.048%	1.05%
89.51%	438.00	440.42	0.552%	0.55%
91.00%	448.00	450.80	0.626%	0.63%
92.30%	463.00	461.36	-0.353%	0.35%
95.61%	513.00	499.29	-2.672%	2.67%
100.00%	643.00	644.71	0.266%	0.27%
AAD %				0.88%

Appendix 4: Predicted results of SG & K_{vis} distribution in Blended condensate

SG distribution in Blended condensate - 100% BNC

vol _{ave} (%)	SG _{Experiment}	SG _{GDM}	D%	[D%]	SG _{NCM}	D%	[D%]	
3.36%	0.576	0.575	-0.18%	0.18%	0.583	1.21%	1.21%	
22.85%	0.654	0.666	1.80%	1.80%	0.654	-0.02%	0.02%	
44.85%	0.730	0.718	-1.64%	1.64%	0.727	-0.37%	0.37%	
62.19%	0.760	0.754	-0.81%	0.81%	0.761	0.07%	0.07%	
76.99%	0.791	0.788	-0.42%	0.42%	0.789	-0.27%	0.27%	
81.14%	0.798	0.799	0.16%	0.16%	0.799	0.19%	0.19%	
82.98%	0.803	0.805	0.16%	0.16%	0.802	-0.12%	0.12%	
85.18%	0.807	0.811	0.49%	0.49%	0.809	0.25%	0.25%	
89.78%	0.836	0.828	-0.88%	0.88%	0.835	-0.03%	0.03%	
96.60%	0.857	0.868	1.31%	1.31%	0.857	-0.01%	0.01%	
Overall	0.732	0.726			0.726			
% AAD				0.79%	% AAD			
E²				0.0069%	E²			
0.0069%					0.0067%			

SG distribution in Blended condensate – 75% BNC and 25% TNC

vol _{ave} (%)	SG _{Experiment}	SG _{GDM}	D%	[D%]	SG _{NCM}	D%	[D%]	
3.17%	0.577	0.577	-0.01%	0.01%	0.584	1.14%	1.14%	
24.97%	0.650	0.660	1.54%	1.54%	0.650	0.00%	0.00%	
48.93%	0.728	0.713	-2.00%	2.00%	0.725	-0.39%	0.39%	
65.30%	0.758	0.749	-1.23%	1.23%	0.758	0.07%	0.07%	
79.32%	0.789	0.784	-0.69%	0.69%	0.787	-0.28%	0.28%	
83.07%	0.795	0.796	0.09%	0.09%	0.797	0.20%	0.20%	
84.80%	0.800	0.802	0.20%	0.20%	0.799	-0.10%	0.10%	
86.79%	0.804	0.809	0.58%	0.58%	0.806	0.22%	0.22%	
90.82%	0.831	0.827	-0.48%	0.48%	0.830	-0.03%	0.03%	
96.90%	0.853	0.870	2.00%	2.00%	0.853	-0.01%	0.01%	
Overall	0.723	0.718			0.718			
% AAD				0.88%	% AAD			
E²				0.0051%	E²			
0.0051%					0.0050%			

SG distribution in Blended condensate – 50% BNC and 50% TNC

vol _{ave} (%)	SG _{Experiment}	SG _{GDM}	D%	[D%]	SG _{NCM}	D%	[D%]	
2.97%	0.578	0.578	-0.01%	0.01%	0.584	1.08%	1.08%	
27.10%	0.648	0.657	1.48%	1.48%	0.648	0.01%	0.01%	
53.02%	0.726	0.711	-2.01%	2.01%	0.723	-0.40%	0.40%	
68.42%	0.755	0.745	-1.45%	1.45%	0.756	0.07%	0.07%	
81.65%	0.787	0.780	-0.87%	0.87%	0.785	-0.28%	0.28%	
85.00%	0.792	0.792	0.01%	0.01%	0.793	0.20%	0.20%	
86.62%	0.796	0.798	0.22%	0.22%	0.795	-0.09%	0.09%	
88.41%	0.800	0.805	0.66%	0.66%	0.802	0.19%	0.19%	
91.87%	0.824	0.823	-0.15%	0.15%	0.824	-0.01%	0.01%	
97.20%	0.849	0.867	2.12%	2.12%	0.849	-0.02%	0.02%	
Overall	0.713	0.709			0.709			
% AAD				0.90%	% AAD			
E²				0.0030%	E²			
0.0030%					0.0034%			

SG distribution in Blended condensate – 25% BNC and 75% TNC

vol _{ave} (%)	SG _{Experiment}	SG _{GDM}	D%	[D%]	SG _{NCM}	D%	[D%]	
2.78%	0.579	0.579	-0.01%	0.01%	0.585	1.03%	1.03%	
29.22%	0.646	0.655	1.40%	1.40%	0.646	0.02%	0.02%	
57.10%	0.723	0.709	-1.92%	1.92%	0.720	-0.39%	0.39%	
71.53%	0.753	0.741	-1.62%	1.62%	0.753	0.07%	0.07%	
83.98%	0.784	0.776	-1.01%	1.01%	0.782	-0.27%	0.27%	
86.93%	0.788	0.787	-0.11%	0.11%	0.789	0.18%	0.18%	
88.44%	0.792	0.793	0.22%	0.22%	0.791	-0.08%	0.08%	
90.03%	0.795	0.801	0.79%	0.79%	0.796	0.16%	0.16%	
92.91%	0.814	0.817	0.34%	0.34%	0.814	0.01%	0.01%	
97.50%	0.843	0.859	1.94%	1.94%	0.843	-0.02%	0.02%	
Overall	0.704	0.701			0.701			
% AAD				0.94%	% AAD			0.22%
E²				0.0014%	E²			0.0021%

SG distribution in Blended condensate – 100% TNC

cum vol _{ave} (%)	SG _{Experiment}	SG _{GDM}	D%	[D%]	SG _{NCM}	D%	[D%]	
2.59%	0.580	0.580	0.03%	0.03%	0.586	0.98%	0.98%	
31.34%	0.644	0.651	1.07%	1.07%	0.644	0.02%	0.02%	
61.19%	0.720	0.706	-1.93%	1.93%	0.717	-0.37%	0.37%	
74.65%	0.750	0.735	-1.95%	1.95%	0.751	0.06%	0.06%	
86.32%	0.780	0.771	-1.14%	1.14%	0.778	-0.24%	0.24%	
88.86%	0.784	0.781	-0.31%	0.31%	0.785	0.13%	0.13%	
90.26%	0.786	0.788	0.20%	0.20%	0.786	-0.09%	0.09%	
91.65%	0.787	0.795	1.08%	1.08%	0.788	0.11%	0.11%	
93.96%	0.799	0.810	1.35%	1.35%	0.799	0.05%	0.05%	
97.81%	0.836	0.851	1.75%	1.75%	0.836	-0.03%	0.03%	
Overall	0.694	0.692			0.692			
% AAD				1.08%	% AAD			0.21%
E²				0.0011%	E²			0.0011%

K_{vis} distribution in Blended condensate – 100% BNC

cum. vol _{ave} (%)	K _{vis,Experiment}	K _{visGDM}	D%	D%	K _{visNCM}	D%	D%	
62.19%	0.620	0.621	0.05%	0.05%	0.622	0.21%	0.21%	
82.98%	1.002	1.071	6.90%	6.90%	0.994	-0.75%	0.75%	
85.18%	1.487	1.432	-3.70%	3.70%	1.509	1.43%	1.43%	
89.78%	2.494	1.962	-21.34%	21.34%	2.480	-0.56%	0.56%	
96.60%	3.882	4.662	20.11%	20.11%	3.875	-0.18%	0.18%	
Overall	0.775	0.776			0.776			
% AAD				10.42%	% AAD			
E²				0.00025%	E²			
0.00010%								

K_{vis} distribution in Blended condensate – 75% BNC and 25% TNC

cum. vol _{ave} (%)	K _{vis,Experiment}	K _{visGDM}	D%	D%	K _{visNCM}	D%	D%	
65.30%	0.708	0.708	0.04%	0.04%	0.709	0.15%	0.15%	
84.80%	1.033	1.088	5.35%	5.35%	1.029	-0.38%	0.38%	
86.79%	1.510	1.433	-5.11%	5.11%	1.527	1.08%	1.08%	
90.82%	2.506	1.952	-22.09%	22.09%	2.493	-0.52%	0.52%	
96.90%	3.913	4.921	25.78%	25.78%	3.905	-0.19%	0.19%	
Overall	0.849	0.850			0.850			
% AAD				11.67%	% AAD			
E²				0.00017%	E²			
0.00007%								

K_{vis} distribution in Blended condensate – 50% BNC and 50% TNC

cum. vol _{ave} (%)	K _{vis,Experiment}	K _{visGDM}	D%	D%	K _{visNCM}	D%	D%	
68.42%	0.808	0.808	0.02%	0.02%	0.809	0.10%	0.10%	
86.62%	1.073	1.109	3.35%	3.35%	1.073	-0.07%	0.07%	
88.41%	1.541	1.435	-6.87%	6.87%	1.553	0.81%	0.81%	
91.87%	2.523	1.945	-22.90%	22.90%	2.511	-0.47%	0.47%	
97.20%	3.950	5.357	35.62%	35.62%	3.943	-0.19%	0.19%	
Overall	0.935	0.936			0.935			
% AAD				13.75%	% AAD			
E²				0.00022%	E²			
0.00004%								

K_{vis} distribution in Blended condensate – 25% BNC and 75% TNC

cum. vol _{ave} (%)	K _{vis,Experiment}	K _{vis,GDM}	D%	{D%}	K _{vis,NCM}	D%	{D%}	
71.53%	0.924	0.924	0.00%	0.00%	0.925	0.06%	0.06%	
88.44%	1.127	1.171	3.87%	3.87%	1.129	0.18%	0.18%	
90.03%	1.583	1.473	-6.96%	6.96%	1.593	0.60%	0.60%	
92.91%	2.547	1.945	-23.64%	23.64%	2.536	-0.42%	0.42%	
97.50%	3.998	5.479	37.06%	37.06%	3.990	-0.19%	0.19%	
Overall	1.034	1.036			1.035			
% AAD				14.30%	% AAD			
E²				0.00047%	E²			
					0.29%			
					0.00002%			

K_{vis} distribution in Blended condensate – 100% TNC

cum. vol _{ave} (%)	K _{vis,Experiment}	K _{vis,GDM}	D%	{D%}	K _{vis,NCM}	D%	{D%}	
74.65%	1.057	1.057	0.00%	0.00%	1.058	0.07%	0.07%	
90.26%	1.202	1.238	3.03%	3.03%	1.204	0.20%	0.20%	
91.65%	1.645	1.516	-7.84%	7.84%	1.658	0.78%	0.78%	
93.96%	2.584	1.955	-24.34%	24.34%	2.578	-0.25%	0.25%	
97.81%	4.059	5.928	46.05%	46.05%	4.043	-0.38%	0.38%	
Overall	1.150	1.154			1.151			
% AAD				16.25%	% AAD			
E²				0.00110%	E²			
					0.34%			
					0.00003%			

Appendix 5: Case Study results

Table 5.1A Feed and distillate products volumetric flow rate of CFU $\alpha = 1$

Feed			Distillate products				
			Cond. Tower			Cond. Stabiliser	
	BNC 11FC501.PV	TNC 11FC502.PV	Top prod 11FC518.PV	S/ stream 11FC514.PV	Bot. prod 11FC507.PV	Top prod 11FC519.PV	Bot. prod 11FC522.PV
V (m3/h)	186	0	71.35	69	44.32	7.58	70.43
%	100	0	38.64	37.36	24.00	9.71	90.29

Table 5.2A: Distillate product ASTM distillations and SG for CFU $\alpha = 1$

Cut Name	Cond. Tower Ovhd	Naphtha product	Cond Tower Btms
Specific gravity	0.6453	0.7574	0.8198
vol (std m3/h)	71.35121494	69.00003704	44.32427897
Volume fraction (%)	38.64%	37.36%	24.00%
Distillation ASTM D86_0.5 vol % [C]	31	82.7	116.7
Distillation ASTM D86_5 vol % [C]	37.2	90.6	138.4
Distillation ASTM D86_10 vol % [C]	38	92.5	143.7
Distillation ASTM D86_20 vol % [C]	39.4	94.8	156.8
Distillation ASTM D86_30 vol % [C]	40.9	97.5	167.4
Distillation ASTM D86_40 vol % [C]	42.5	100.4	179.6
Distillation ASTM D86_50 vol % [C]	44.5	103.8	193.9
Distillation ASTM D86_60 vol % [C]	47.2	108.6	208.4
Distillation ASTM D86_70 vol % [C]	50.8	114.4	225.9
Distillation ASTM D86_80 vol % [C]	56.2	123.2	245.9
Distillation ASTM D86_90 vol % [C]	64.7	138.1	273.5
Distillation ASTM D86_95 vol % [C]	69.8	152.4	307.5
Distillation ASTM D86_99.5 vol % [C]	76.4	175.1	348

Table 5.1B: Feed and distillate products volumetric flow rate at $\alpha = 0.5$

Feed			Distillate products				
			Cond. Tower			Cond. Stabiliser	
	BNC	TNC	Top prod	Naphtha	Bott. prod	Top prod	Bott. prod
Flow rate m3/h	93	93	89.90	62.5	33.46	5.15	93.96
%	50	50	48.37	33.63	18.00	5.20	94.80

Table 5.2B: Distillate product ASTM distillations and SG for CFU $\alpha = 0.5$

Feed			Distillate products				
			Cond. Tower			Cond. Stabiliser	
	BNC	TNC	Top prod	Naphtha	Bott. prod	Top prod	Bott. prod
Flow rate m3/h	186	0	77.45	65	42.74	8.41	77.11
%	100	0	41.82	35.10	23.08	9.83	90.17

Table 5.3B-1 ASTM distillation & SG for Cond. Tower distillate Products at $\alpha = 0.5$

Cut Name	Cond. Tower Ovhd	Naphtha product	Cond Tower Btms
Specific gravity	0.65	0.75	0.82
vol (std m3/h)	89.90	62.50	33.46
Volume fraction (%)	48.37%	33.63%	18.00%
Distillation ASTM D86_0.5 vol % [C]	24.20	78.5	136.6
Distillation ASTM D86_5 vol % [C]	37	89.5	149.70
Distillation ASTM D86_10 vol % [C]	37.90	91.60	155.30
Distillation ASTM D86_20 vol % [C]	39.20	94.70	165.60
Distillation ASTM D86_30 vol % [C]	40.70	97.60	176.70
Distillation ASTM D86_40 vol % [C]	42.5	101.00	188.00
Distillation ASTM D86_50 vol % [C]	44.80	105.00	199.90
Distillation ASTM D86_60 vol % [C]	60	109.5	215.80
Distillation ASTM D86_70 vol % [C]	51.5	115.30	234.20
Distillation ASTM D86_80 vol % [C]	58.20	123.60	254.10
Distillation ASTM D86_90 vol % [C]	69.40	136.20	281.5
Distillation ASTM D86_95 vol % [C]	78.30	151.70	311.80
Distillation ASTM D86_99.5 vol % [C]	91.20	176.40	349.50

Table 5.3B-2 ASTM distillation & SG for Cond. Tower distillate Products at $\alpha = 1$

Cut Name	Cond. Tower Ovhd	Naphtha product	Cond Tower Btms
Specific gravity	0.66	0.76	0.81
vol (std m3/h)	77.45	65.00	42.74
Volume fraction (%)	41.82%	35.10%	23.08%
Distillation ASTM D86_0.5 vol % [C]	21.70	81.40	128.5
Distillation ASTM D86_5 vol % [C]	37.5	90.10	143.70
Distillation ASTM D86_10 vol % [C]	38.70	92	151.10
Distillation ASTM D86_20 vol % [C]	40.70	95.10	160.60
Distillation ASTM D86_30 vol % [C]	42.80	98.20	170.70
Distillation ASTM D86_40 vol % [C]	45	101.80	181.60
Distillation ASTM D86_50 vol % [C]	47.80	105.80	193.60
Distillation ASTM D86_60 vol % [C]	51.5	110.90	208.80
Distillation ASTM D86_70 vol % [C]	56.60	117.30	226.20
Distillation ASTM D86_80 vol % [C]	70.10	126	245.10
Distillation ASTM D86_90 vol % [C]	76.20	140.60	270.90
Distillation ASTM D86_95 vol % [C]	84.10	154.60	297.10
Distillation ASTM D86_99.5 vol % [C]	95.30	177.10	328.40

Table 5.3C-1 ASTM conversion to TBP for all distillate products, $\alpha = 0.5$

Vol. %	Top product		Naphtha		Bottom product	
	ASTM D86	TBP	ASTM D86	TBP	ASTM D86	TBP
0.5	24.20	-1.52	78.50	49.29	136.60	98.72
10	37.90	26.83	91.60	76.89	155.30	132.92
30	40.70	35.50	97.60	91.86	176.70	170.16
50	44.80	43.85	105.00	105.25	199.90	203.59
70	51.50	54.67	115.30	120.64	234.20	244.87
90	69.40	77.92	136.20	146.78	281.50	293.30
100	91.20	101.35	176.40	211.50	349.50	448.23

Table 5.3C-2 ASTM conversion to TBP for all distillate products, $\alpha = 1$

Vol. %	Top product		Naphtha		Bottom product	
	ASTM D86	TBP	ASTM D86	TBP	ASTM D86	TBP
0.5	21.70	-6.59	81.40	52.77	128.50	90.64
10	38.70	25.70	92.00	77.06	151.10	128.97
30	42.80	37.10	98.20	92.39	170.70	163.93
50	47.80	46.88	105.80	106.07	193.60	197.02
70	56.60	60.41	117.30	122.92	226.20	236.62
90	76.20	85.31	140.60	151.30	270.90	283.02
100	95.30	104.12	177.10	206.43	328.40	400.29