

PETRONASTECHNICALSTANDARDS

THERMODYNAMIC PROPERTY PACKAGE SELECTION

PTS 20.00.10.37

OCTOBER 2011



©2011 PETROLIAM NASIONAL BERHAD (PETRONAS)

All rights reserved. No part of this document may be reproduced, stored in a retrieval system or transmitted in any form or by any means (electronic, mechanical, photocopying, recording or otherwise) without the permission of the copyright owner.

PTS Circular 2011	PETRONAS 
PTS No:	20.00.10.37
PTS Title:	Thermodynamic Property Package Selection

This revision of PTS 20.00.10.37 - Thermodynamic Property Package Selection (October 2011, Revision 2) has been updated to incorporate information from PTS 20.00.10.10 – Basic Data and Phase Behavior Methods (April 2003, Revision 0), PETRONAS Lessons Learnt, Best Practice and new information issued by relevant industry code and standards. All updates in the document are highlighted in italic font.

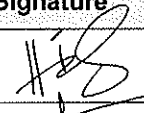
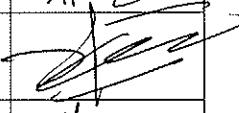
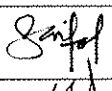
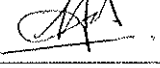
The custodian of this PTS is:

Name: Hasnor Hassaruddin b Hashim

Tel. No.: 03 – 2783 6476

Please direct any questions regarding this PTS to the above-named

Document Approval

	Name	Designation	Date	Signature
Prepared	Noorhidayah Hussein	Process Simulation & Optimization Engineer	23 Sept 2011	
Reviewed	Hasnor Hassaruddin Hashim	Principal Engineer, Process Simulation & Optimization	3 Oct 2011	
Approved	Shahrul Azman Zainal Abidin	Custodian Engineer, Process Simulation & Optimization	17 Oct 2011	
Verified	Shahrul Izan Bakti b A Aziz	Senior Manager, Process Engineering, Engineering, GTS	27/10/11	
Verified	Saifol Muallim b Ahmad Yahaya	General Manager, Engineering, GTS	31/10/11	
Endorsed	Pau Kiew Huai	Senior General Manager, GTS	1.11.11	

Revision History

Rev. No.	Reviewed by	Approved by	Date
0	Shahrul Azman b Zainal Abidin/ Hasnor Hassaruddin b Hashim	Shahrul Azman b Zainal Abidin	11 Feb 2009
1	Hasnor Hassaruddin b Hashim	Shahrul Azman b Zainal Abidin	14 Oct 2011

PREFACE

PETRONAS Technical Standards (PTS) publications reflect the views, at the time of publication, of PETRONAS OPU/Divisions.

They are based on the experience acquired during the involvement with the design, construction, operation and maintenance of processing units and facilities. Where appropriate they are based on, or reference is made to, national and international standards and codes of practice.

The objective is to set the recommended standard for good technical practice to be applied by PETRONAS' OPU in oil and gas production facilities, refineries, gas processing plants, chemical plants, marketing facilities or any other such facility, and thereby to achieve maximum technical and economic benefit from standardization.

The information set forth in these publications is provided to users for their consideration and decision to implement. This is of particular importance where PTS may not cover every requirement or diversity of condition at each locality. The system of PTS is expected to be sufficiently flexible to allow individual operating units to adapt the information set forth in PTS to their own environment and requirements.

When Contractors or Manufacturers/Suppliers use PTS they shall be solely responsible for the quality of work and the attainment of the required design and engineering standards. In particular, for those requirements not specifically covered, it is expected of them to follow those design and engineering practices which will achieve the same level of integrity as reflected in the PTS. If in doubt, the Contractor or Manufacturer/Supplier shall, without detracting from his own responsibility, consult the owner.

The right to use PTS rests with three categories of users:

- 1) PETRONAS and its affiliates.
- 2) Other parties who are authorized to use PTS subject to appropriate contractual arrangements.
- 3) Contractors/subcontractors and Manufacturers/Suppliers under a contract with users referred to under 1) and 2) which requires that tenders for projects, materials supplied or - generally - work performed on behalf of the said users comply with the relevant standards.

Subject to any particular terms and conditions as may be set forth in specific agreements with users, PETRONAS disclaims any liability of whatsoever nature for any damage (including injury or death) suffered by any company or person whomsoever as a result of or in connection with the use, application or implementation of any PTS, combination of PTS or any part thereof. The benefit of this disclaimer shall inure in all respects to PETRONAS and/or any company affiliated to PETRONAS that may issue PTS or require the use of PTS.

Without prejudice to any specific terms in respect of confidentiality under relevant contractual arrangements, PTS shall not, without the prior written consent of PETRONAS, be disclosed by users to any company or person whomsoever and the PTS shall be used exclusively for the purpose they have been provided to the user. They shall be returned after use, including any copies which shall only be made by users with the express prior written consent of PETRONAS.

The copyright of PTS vests in PETRONAS. Users shall arrange for PTS to be held in safe custody and PETRONAS may at any time require information satisfactory to PETRONAS in order to ascertain how users implement this requirement.

TABLE OF CONTENT

1	INTRODUCTION.....	6
1.1	SCOPE.....	6
1.2	DISTRIBUTION, INTENDED USE AND REGULATORY CONSIDERATIONS.....	6
1.3	DEFINITIONS.....	6
1.4	ABBREVIATIONS.....	7
1.5	CROSS REFERENCES.....	7
1.6	CHANGES FROM PREVIOUS EDITION.....	8
2	EXCEPTIONS/AMMENDMENTS.....	9
3	GLOSSARY OF TERMS.....	9
4	THEORY OF PROPERTY PACKAGE.....	10
4.1	GENERAL.....	10
4.2	FUTURE FOR SIMULATION/DATA.....	12
4.3	COMMERCIAL PROGRAM.....	15
4.4	FUNDAMENTALS OF THERMODYNAMICS.....	16
4.5	PHASE BEHAVIOR METHOD.....	20
5	DATA AVAILABILITY.....	34
5.1	INTRODUCTION.....	34
5.2	MISSING COMPOUND.....	34
5.3	MISSING/UPGRADING COMPOUND PROPERTY/PARAMETER.....	34
5.4	MISSING/UPGRADING BINARY PARAMETERS.....	34
5.5	DATA SOURCES.....	35
6	PHYSICAL PROPERTY METHOD.....	35
6.1	THERMODYNAMIC PROPERTY METHOD.....	35
6.2	TRANSPORT PROPERTY METHOD.....	38
6.3	MISCELLANEOUS PROPERTY METHOD.....	40
7	PSEUDO COMPONENT CHARACTERIZATION.....	40
8	ANALYTICAL DATA.....	41
8.1	INTRODUCTION.....	41
8.2	DOWN-STREAM CRUDE OIL.....	41
8.3	UPSTREAM OIL AND NATURAL GAS.....	41
9	PHASE BEHAVIOR IN AQUEOUS HYDROCARBON SYSTEMS.....	41
9.1	GENERAL.....	41
9.2	HYDROCARBON/WATER.....	42
9.3	HYDROCARBON/METHANOL/WATER.....	42
9.4	HYDROCARBON/GLYCOL/WATER.....	43
10	SYSTEM RECOMMENDATIONS.....	43
10.1	GENERAL.....	43
10.2	RECOMMENDED METHOD FOR PETRONAS APPLICATION.....	43
10.3	PROPERTY PACKAGE SELECTION.....	44
10.4	GUIDE ON SELECTING A THERMO PACKAGE.....	44
10.5	PETRONAS RECOMMENDED PROPERTY PACKAGE.....	45
11	PETRONAS LESSON LEARNT.....	46
12	PETRONAS BEST PRACTICE.....	47
13	REFERENCES.....	48
14	BIBLIOGRAPHY.....	48

LIST OF TABLES

Table 1: Important factors in basic data method selection	10
Table 2: Ideal Property Package Description.....	21
Table 3: Equation of States (EOS) Description.....	23
Table 4: Activity Coefficients Model Description	28
Table 5: Special Property Package Description.....	30
Table 6: Liquid Density Calculation in Process Simulation Software	36
Table 7: Viscosity Calculation Method based on Property Package	39
Table 8: Thermal Conductivity Calculation Method based on Property Package.....	39
Table 9: Surface Tension Calculation Method based on Property Package	40
Table 10: Property Package in PETRONAS OPUs simulation cases	45
Table 11: Property Package recommended for various hydrocarbon system.....	46

LIST OF FIGURES

Figure 1: Selection of Thermodynamic Package in iCON	44
Figure 2: Guide on Property Package Selection.....	44

1 INTRODUCTION

1.1 SCOPE

This PTS specifies requirements and gives recommendations for the selection of thermodynamic property package for any process simulation work particularly using iCON, PETRONAS in-house process simulation software. The party responsible for the process design and process optimization work prepares these recommendations of this property package selection.

The requirements and recommendations in this PTS are independent of the tools with which the simulation models are produced. However, it is advised that iCON (PETRONAS Process Simulation Software) is used to generate the process model to aid models accessibility. If other process simulation software is used, it shall be endorsed by GTS Process Simulation & Optimization Custodian Engineer and a copy of the software shall be made available to PETRONAS.

1.2 DISTRIBUTION, INTENDED USE AND REGULATORY CONSIDERATIONS

Unless otherwise authorized by PETRONAS, the distribution of this PTS is confined to companies forming part of PETRONAS or managed by a Group company, and to Contractors nominated by them.

This PTS is intended for use in oil refineries, gas plants, chemical plants, exploration and production facilities and where applicable, supply/marketing installations. When PTSs are applied, a Management of Change (MOC) process should be implemented. This is of particular importance when existing facilities are to be modified.

If national and/or local regulations exist in which some of the requirements may be more stringent than in this PTS, the Contractor shall determine by careful scrutiny which of the requirements are the more stringent and which combination of requirements will be acceptable as regards to safety, environmental, economic and legal aspects. In all cases the Contractor shall inform the Principal of any deviation from the requirements of this PTS which is considered to be necessary in order to comply with national and/or local regulations. The Principal may then negotiate with the authorities concerned with the object of obtaining agreement to follow this PTS as closely as possible.

1.3 DEFINITIONS

The **Contractor** is the party that carries out all or part of the design, engineering, procurement, construction, commissioning or management of a project or operation of a facility. The Principal may undertake all or part of the duties of the Contractor.

The **Manufacturer/Supplier** is the party that manufactures or supplies equipment and services to perform the duties specified by the Contractor.

The **Principal** is the party that initiates the project and ultimately pays for its design and construction. The Principal will generally specify the technical requirements. The Principal may also include an agent or consultant authorized to act for, and on behalf of, the Principal.

The word **shall** indicate a requirement.

The word **should** indicate a recommendation.

1.4 ABBREVIATIONS

<i>API</i>	<i>American Petroleum Institute</i>
<i>BIP</i>	<i>Binary Interaction Parameter</i>
<i>C20</i>	<i>Hydrocarbon with carbon number 20, eicosane</i>
<i>CPA</i>	<i>Cubic Plus Association equation of state</i>
<i>DIPPR</i>	<i>Design Institute for Physical Property Data</i>
<i>EAS</i>	<i>Engineering Analysis Suite</i>
<i>EoS</i>	<i>Equation of State</i>
<i>GOR</i>	<i>Gas Oil Ratio</i>
<i>GP(S)A</i>	<i>Gas Processors (Suppliers) Association</i>
<i>GUI</i>	<i>Graphical User Interface</i>
<i>IUPAC</i>	<i>International Union of Pure and Applied Chemistry</i>
<i>LLE</i>	<i>Liquid-Liquid Equilibria</i>
<i>LNG</i>	<i>Liquefied Natural Gas</i>
<i>MW</i>	<i>Molecular Weight</i>
<i>NGL</i>	<i>Natural Gas Liquids</i>
<i>NIST</i>	<i>National Institute of Standards and Technology</i>
<i>NRTL</i>	<i>Non Random Two Liquid activity coefficient model</i>
<i>PO</i>	<i>Propylene Oxide</i>
<i>PR</i>	<i>Peng-Robinson Equation of State</i>
<i>PVT</i>	<i>Pressure, Volume and Temperature</i>
<i>SG</i>	<i>Specific Gravity</i>
<i>SRK</i>	<i>Soave-RedlichKwong Equation of State</i>
<i>TBP</i>	<i>True Boiling Point</i>
<i>TRC</i>	<i>Thermodynamics Research Center</i>
<i>VLE</i>	<i>Vapor-Liquid Equilibria</i>
<i>VLLE</i>	<i>Vapor-Liquid-Liquid Equilibria</i>
<i>VMG</i>	<i>Virtual Materials Group</i>
<i>VMGThermo</i>	<i>Virtual Materials Group Property Package System</i>

1.5 CROSS REFERENCES

Where cross-references to other parts of this PTS are made, the referenced section number is shown in brackets.

1.6 CHANGES FROM PREVIOUS EDITION

The previous edition of this PTS was Feb 2009. Other than editorial editions, the following are the main changes since that edition:

Old Section	New Section	Change
N/A	3	Added glossary of terms as reference
3	4.1	Added general information related to property package and factors that affect the selection of property package.
	4.2	Added future simulation data information
	4.3	Added list of commercial simulation program in market which is currently used in PETRONAS
	4.4	Added fundamentals of thermodynamics as theory references
	4.5	Added phase behavior method information and the list of simulation program which have similar phase behavior method calculation
	5	Added options of data availability for simulation and how to deal with data unavailability.
	6	Added physical property method of calculation which includes thermodynamic property method and transport property method.
	7	Added pseudo component characterization and other PTS as reference
	8	Added analytical data used for simulation which comprises of downstream crude oil, upstream crude oil, and natural gas.
	9	Added phase behavior in aqueous hydrocarbon systems which include hydrocarbon in water, hydrocarbon in methanol and water, hydrocarbon in glycol and water
5	10	Rearrange section 5 in previous version of PTS to include brief introduction on recommended system in PETRONAS

2 EXCEPTIONS/AMMENDMENTS

Nil

3 GLOSSARY OF TERMS

Basic Data – Comprises all elements (data as well as programs) that are required to describe and predict the phase behavior and physical properties of chemical mixtures at any specific condition.

Binary interaction coefficient/parameter (BIP) – A constant that accounts for the deviation from ideality for two component mixtures. These are specific to one equation of state as they are calculated by regression of measured data. For example, coefficients used in APR are quite different from those used in SRK. The coefficients used in a liquid activity method are essentially regression constants used to calculate the liquid activity coefficient.

CPA – Cubic Plus Association. This equation of state combines a simple cubic (usually SRK, but any cubic can be used) with an association term inspired by the SAFT family of equations of state. The basic idea is that the model will reduce to a cubic equation of state for non-associating components while association is taken into account for associating compounds such as water, alcohols glycols and others. The association modeling is usually concerned with hydrogen bonding effects. This model has received significant attention in the literature (Kontogeorgis et al, 1996) and further developed, notably in Denmark. The model has some attractive features such as qualitatively reasonable predictions (without interaction parameters) for some complex behavior such as mutual solubilities of water/hydrocarbon systems. The model also has some significant drawbacks such as the loss of cubic form for associating systems, more adjustable parameters for pure components and, from a correlative point of view no distinct advantage over Gibbs Excess based mixing rules.

Dalton's Law – The pressure exerted by a mixture of gases is equal to the sum of the partial pressures of the component gases.

Distribution coefficient or K-value – Coefficient or ratio that describes the distribution of a component between phases and is the keystone of all phase calculations. The higher the value, the more volatile the component. A simple concept, but complicated function of pressure, temperature and composition.

Equation of state – An equation that describes the relationship between pressure, temperature, and molar volume for any homogenous fluid at equilibrium.

Fugacity - Translated literally it means escaping tendency and is an indication of the ability of a component to move between phases. At equilibrium, the fugacities of all phases are equal. For ideal gases where intermolecular interaction is, by definition, negligible, the fugacity and partial pressure of a component are identical.

Henry's Law - The partial pressure developed by a solute in a solvent is directly proportional to the mole fraction of the solute in the solvent. This is only true for low concentrations of solute.

Ideal Gas - An ideal gas is one where the volume occupied by the molecules is infinitesimal when compared to the total volume occupied by the gas, i.e. the intermolecular force of attraction approaches zero.

NIST – National Institute of Standards and Technology. NIST is a division of the United States Department of Commerce and is dedicated to the production of world class standards for the measurement and calculation of physical properties. Thermodynamic models developed for use in iCON/VMGSim are based on NIST high quality, evaluated thermodynamic and physical property data developed by TRC, a division of NIST's Thermophysical Properties Division

Liquid activity coefficient - The ratio of the fugacity of a component in a mixture and in its pure state, at the same physical conditions, divided by its mole fraction in the mixture.

Parachor- A parameter describing the influence that a density difference between phases has on surface tension

Principle of corresponding states - All gases when compared at the same reduced temperature and pressure have approximately the same compressibility factor and all deviate from ideality to the same degree.

Raoult's Law - The vapor pressure exerted by a component in ideal solution condition is directly proportional to its mole fraction.

TRC – Thermodynamics Research Center is a division of NIST's Thermophysical Properties Division dedicated to the collection and critical evaluation of physical property data.

4 THEORY OF PROPERTY PACKAGE

4.1 GENERAL

Reliable estimation of phase behavior and physical properties of mixtures is essential for the analysis and simulation of oil, gas and chemical processes. The data, models, and methods required for this purpose are collectively known as basic data. Various methods are available for estimation of any given property. These basic data methods maybe different in the thermodynamic path followed to calculate the property, selected models or databanks, or in all of these. Making an appropriate choice for a specific problem is important. Various factors, listed in Table 1, determine which methods are more suitable than others for particular cases.

Table 1: Important factors in basic data method selection

Factors	Example
Available/preferred simulation program	i) iCON ii) VMGSim iii) HYSYS/UniSIM/Petro-SIM iv) Aspen Plus v) Pro/II
Type of system	Pure component, binary or multi-component mixture
Kind of physical properties	Thermodynamic, transport, surface
Nature of the substances	Polar, non-polar, electrolytes, polymers, solids
Conditions of the system or process	Sub-or super-critical temperature, low or high pressure, dilute or concentrated mixture, expected phase behavior
Required accuracy	Screening or design purposes, importance of parameters
Availability of experimental data	Fit or estimate missing parameters
Computational speed	Simple or complex model

Usually it is necessary to compute pure component properties as well as mixture properties using one of the simulation programs. For most pure component properties computations, the choice of models/correlations is fairly straightforward, because of the availability of pure component databanks containing specific correlations for the required properties. Even though pure component computations are simpler, the reader should keep in mind that accurate values for pure component properties such as vapor pressures and densities are of paramount importance for process design and also for the development of mixture models. Inaccurate vapor pressures for example, irrespective of how good from a theoretical point of view a mixture model is, will produce incorrect results. Also note that accurate pure component properties coming directly from a database do not correspond to accurate values from a mixture model.

For example, a component may have accurate vapor pressures and liquid densities coming from the pure component database (say from an Antoine equation and a Rackett type equation respectively) but the mixture model (say SRK) may provide rather different predictions for these pure component properties. These are limitations inherent of the selected mixture model and must be checked before time is invested in the development of complex simulation models.

For the computation of mixture properties however, few such databanks exists and the choice of the appropriate model is complicated by the fact that all models have limitations based on the factors listed in Table 1. In other words, it is impossible to provide accurate mixture data for all possible mixtures of interest and available experimental mixture data (for example VLE data) must be extended through the use of adequate thermodynamic models such as equations of state and activity coefficient models.

The main tool for process simulation in PETRONAS is iCON, the PETRONAS version of VMGSim, which is equipped with a large number of standard basic data methods via VMGThermo. There are also other process simulation softwares which are used for selected cases i.e. HYSYS, Aspen Plus and PRO/II. The usage of other process simulation software is subjected to approval from Process Simulation and Optimization Custodian Engineer.

Although the manuals accompanying these tools provide descriptions and application ranges of the individual methods, it is not an easy task to select a basic data method suitable for the calculation of the required properties of the mixture at hand.

In practice, even though designers may use a number of personal guidelines, there is no general understanding of when to use which basic data method. As a result, a user may choose a basic data method that is not the most appropriate for the specific application. This may result in seemingly converged and accurate output that contains hidden mistakes.

Common traps are extrapolating data outside the range of fitted parameters (temperature, pressure) use of model compounds to mimic certain components, etc.

The GUI hypertext help facilities in these tools assist users in dealing with more or less standard problems. In fact, this is common to all the knowledge-based ('expert') systems that have been developed at academia over the last few years.

Irrespective of what these systems say, always strive to understand the basic thermodynamic model and check its accuracy against good quality experimental data before starting a large, costly simulation project. Basic checks such as vapor pressures, liquid densities, and VLE are always recommended. Well-developed property packages such as APR and APR-NG have extensive validation suites and if no validation is available VMG can be contacted for a quick availability check of data in the open literature.

4.2 FUTURE FOR SIMULATION/DATA

From a process engineering point of view there remains significant polishing left in the models commonly used in process simulators, but it is also true that some basic characteristics of currently used models will remain well into the 21st Century simulation tools. We will divide this section into pure component modeling, excess properties, energy, volume and advanced estimation.

4.2.1 PURE COMPONENT MODELING

Considerable progress was achieved over the last 10 years in the development of reliable pure component properties. Pure component properties are the fundamental stepping stone for the development of mixture models. Pure component properties are natural boundary conditions for mixture behavior and inaccuracies on pure component properties cause unavoidable distortions on mixture models (Agarwal et al, 1999).

The development of NIST's TDE (Thermo Data Engine, <http://www.nist.gov/srd/nist103b.cfm>) now provides a strong theoretical background for the development of pure component properties. TDE contains not only all publicly available data for a pure compound but also contains the necessary evaluation of data in terms of uncertainties for each data point. This in turn allows a rational evaluation of physical property values and proper weighting of data when performing data regression and parameter evaluation. This detail is of fundamental importance for the development of truly rigorous physical property databases and the reason why Virtual Materials Group was the first process simulation company to join TRC in 1999 and be able to provide property package validations based exclusively on evaluated data.

Virtual Materials Group is now in the process of reengineering its pure component physical property databases to include only evaluated physical property data and correlations based on TDE, with the necessary uncertainty information for each data point. This effort is connected with VMG's goal of providing on-demand quality information to process engineers using VMGThermo in a simple and intuitive way.

4.2.2 EXCESS PROPERTIES

Excess properties are necessary to model the phase behavior and mixture properties. The most famous excess properties are the activity and fugacity coefficient, used extensively for the determination of phase equilibrium, and by default providing estimates for other excess properties such as excess volumes and excess enthalpies. The modeling of activity or fugacity coefficients is nothing more, nothing less than the modeling of the Gibbs free energy and this effort has received a large amount of attention for the last 100 years and will continue to be an important activity for chemical engineers.

Cubic based equations of state will continue to be used for process engineering calculations. Although interesting developments continue to appear in the scientific literature, most notably the SAFT family of equations of state, the fact of the matter remains that, for reliable phase equilibrium computations cubic equations of state, properly parameterized for accurate calculation of critical temperatures, pressures and vapor pressures and coupled with a reliable mixing rule, such as Gibbs excess based mixing rules, provide a formidable platform for accurate data regression and data extension. Virtual Materials Group introduced some of these developments in the APR, APRNG and GEPR models and is now revising these models with the goal of producing a "universal" equation of state that will be used for natural gas, refining and chemical processing. This effort is now possible thanks to the latest versions of TDE, which allow for a rational exploration of the technical literature related to vapor-liquid and liquid-liquid equilibrium and the associated estimated uncertainty of the data.

Non-Cubic equations of state such as SAFT show how a more theoretically based model can be effectively used for process calculations. Unfortunately, for conventional process engineering calculations the model shows little improvement over properly parameterized cubics and model parameters have to be determined based on vapor pressure and liquid density data. Usually the pure component critical pressure and temperature are not

reproduced exactly or the use of critical conditions produce an equation of state that does not provide proper vapor pressures and liquid densities. The equation of state is also significant more complex, takes longer to solve and can produce unrealistic pressure/temperature diagrams. These shortcomings will be worked out in the future and the fundamental strength of this type of modeling – better theoretical basis and natural handling of hydrogen bonding association – will shine. At this moment, unless an exceptional problem is at hand (for example high pressure polymer modeling) this type of model is not necessary for sound process engineering calculations.

“Quasi-Cubic” models such as CPA (cubic plus association) show an interesting compromise between practicality, accuracy and theory. This approach combines the SAFT association term with the simplicity of cubic equations of state and provides a more theoretically based model for the simulation of alcohol/water systems, important for the natural gas industry. The model is not cubic anymore for associating systems and requires special care for its solution although reliable methods seem to have been reported in the literature. When association is present accurate pure component critical points are not calculated anymore (for example it is known that the predicted critical pressure of water will be off by several atmospheres). The model shows promise by providing qualitatively reasonable estimates for VLE and LLE behavior of alcohol/hydrocarbon systems without adjustable parameters. We are carefully evaluating this type of model although no clear advantage from a correlation point of view was found when dealing with complex polar systems.

Activity coefficient models are plentiful and have reached maturity from a process engineering point of view. From the many available models, NRTL and UNIQUAC are the recommended correlating shapes. When interaction parameters are properly developed these models provide powerful correlative platforms and virtually any chemical process can be accurately modeled using these equations. In order to use these models for process calculations models for volume and energy must be provided and they are therefore not adequate for high pressure applications. Commonly ideal gas phase is assumed although an associating model (Hayden and O’Connell for example) must be used for carboxylic acid systems and a simple cubic like APR can be used for the gas phase. This is usually done not to increase the VLE accuracy but rather to increase the accuracy of compressor models. For associating systems the use of appropriate vapor model is a must since incorrect fluid densities will be calculated otherwise.

Activity coefficient models have been extended into predictive models thanks to group contribution methods such as UNIFAC and these are an important tool in the process engineer’s toolbox.

In addition, theoretically based activity coefficient models such as COSMO-RS are important theoretical developments and allow for reasonably accurate estimates of activity coefficients for complex systems not yet incorporated into the UNIFAC framework.

4.2.3 ENERGY AND VOLUME

The simplicity of the cubic model, important for process engineering and efficient use of data collected during hydrocarbon characterization efforts (either from a natural gas, refining or bitumen processing points of view) also limits its accuracy, especially when tasked with volumetric and energy computations such as volumes, enthalpies and entropies, either for pure components or mixtures. Although these estimations are frequently adequate for process engineering applications, more specialized applications involving polar and non-polar compounds in the same mixture, very high pressure applications such as acid gas injection, advanced compressor design require accurate physical properties that are estimated using the cubic form and therefore several times of questionable accuracy. Typical examples are volumes at very high pressures, heat capacities and speeds of sound.

There’s still room for some improvement in the quality of volumetric predictions for cubic equations of state, most notably the use of temperature dependent volume translation. This simple method is adequate for the correlation of liquid density data used for refinery models and will remove the need to use correlations like Rackett or COSTALD for refinery

applications. Unfortunately this refinement does not improve significantly volumetric predictions at very high pressures nor other volumetric and energy derived properties such as enthalpies, heat capacities and speeds of sound.

It is known for many years that the volume dependency of real fluids is not truly cubic in nature and specialized equations of state have been developed to address this issue. It is our belief that the most powerful solution related to practical process engineering is the use of a cubic equation of state for phase equilibrium calculations and the use of a high quality non-cubic for the calculation of volumetric and energy physical properties if the final engineering application truly requires extra accuracy. Useful non-cubic equations of state for this type of application are the GERG equation and Soave's version of BWR (SBWR). There are two important issues related to the use of these equations of state coupled with cubics for phase equilibrium calculations that user should be aware of:

- The energy and volume models are inconsistent with the phase equilibrium model. In another words, in the vicinity of the critical point (assuming that both models are properly parameterized and accurate away from the critical region) there is a likelihood of a model predicting a certain phase type – say liquid – while the other model may predict another phase type – say vapor – thus creating problems with the energy or entropy balances.
- Non-cubic equations of state are notorious for not predicting good water and mixtures containing water physical and mixture properties. This may be a significant problem when dealing with natural gas and refinery mixtures.

4.2.4 CONCLUSIONS

At the time of this writing the thermodynamic framework that will be available through VMGThermo, superseding the current models will be:

- Validated cubic equation of state providing accurate vapor pressures and liquid densities for essentially all chemicals in VMG's pure component database
- Validated cubic equation of state providing accurate VLE predictions for all available evaluated vapor-liquid equilibrium data in the open literature using an advanced mixing rule (likely Gibbs excess based).
- Validated cubic equation of state providing accurate VLLE predictions for special systems such as water/H₂C, water/H₂C/alcohols and other systems of special interest for the natural gas and refining industries
- Automatic interaction parameter regression for this new equation of state based on UNIFAC or COSMO-RS thus providing the best theoretical grounding for process engineering model out of the box
- Option to use SBWR or GERG for volume and energy computations for special applications (e.g. vessel depressurization and compressor acoustic analysis).

The timeframe for complete implementation of this solution is estimated to be 5 years.

4.3 COMMERCIAL PROGRAM

The following are the list of commercial process simulation software that is currently/have been used in PETRONAS but not limited to:

1. **API Technical Data Book** – An electronic version of American Petroleum Institute (API) Technical Databook Petroleum Refining marketed by EPCON International. It provides methods for distillation inter-conversions, estimating physical properties of refinery streams and splitting petroleum fractions into pseudocomponents
2. **Aspen Plus by AspenTech** – This is the standard steady state process simulation program, equipped with a GUI used in PP(M)SB. Current version released is Version 7.3 which includes access experimental mixture property and phase equilibrium data for over 30,000 component pairs and possesses large databases of pure components and phase equilibrium data for conventional chemicals, electrolytes, solids and polymers
3. **Dynsim by Invensys** – used in OTS as Dynamic Engine (MLNG3)
4. **HYSYS by AspenTech** – is a fully integrated steady state and dynamic process simulation program. Widely used for process modeling for conceptual design, optimization, business planning, asset management, and performance monitoring for oil and gas production, gas processing, petroleum refining and air separation industries. Current version released is Version 7.3 which enables direct links from Aspen HYSYS to Aspen Energy Analyzer, improved high pressure results from hydrate formation utility and new greenhouse gas emissions reporting. HYSYS Steady State is mainly used in PCSB Development Division (DD) while HYSYS Dynamic is used as OTS Dynamic Engine in AMSB
5. **INDISS by RSI** – used in OTS as Dynamic Engine (EMSB, PASB, GPP-A&B)
6. **OLGA by SPT** – is a dynamic process simulation tool for engineering the flow of oil, water and gas in wells, pipelines, and receiving facilities. Pipeline flow assurance and well dynamics in OLGA ensure technical, operational and HSE integrity during design and operation of production systems throughout the entire life cycle.
7. **Petro-SIM by KBC** – is a steady state process simulation tool which is used for detailed unit modeling and monitoring as well as plant-wide simulation. In PETRONAS, Petro-SIM is used in VIP projects
8. **PIPESIM by Schlumberger** – is a steady state, multiphase flow simulator for the design and diagnostic analysis for oil and gas production system. It can model multiphase flow from the reservoir to the wellhead. It is also analyzes flowline and surface facility performance to generate comprehensive production system analysis.
9. **Pro/II by Invensys** – is a steady state simulator enabling improved process design and operational analysis. It is designed to perform rigorous mass and energy balance calculations for a wide range of chemical processes. Pro-II is used in MLNG.
10. **UniSIM by Honeywell** – used in OTS as Dynamic Engine (PP(M)SB MG-3, MLNG1&2, PM(L)SB)
11. **VMGSim by Virtual Materials Group Inc.** – is available for both steady state and dynamic process simulation. VMGSim uses VMGThermo as the heart of the simulation, which have comprehensive property package engine includes support for chemically reactive systems, oil and rigorous multiphase flash, combined with extensive selection of equations of state and activity coefficient model. It is also can be used for crude oil characterization. iCON is the PETRONAS version of VMGSim which is currently widely used in PETRONAS especially in upstream and gas processing industries