

## Thermodynamic Properties for the Simulation of Crude Oil Primary Refining

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### ABSTRACT

Commonly, the use of simulators in the industry is performed without having a proper theoretical support. Sometimes this situation is a consequence of both, lack of time and the dairy dynamism required in the refinery industries. Particularly, the application of thermodynamic models is often not properly considered for the specific process under analysis. An undesirable fact can appear, for example, when a wrong properties package is chosen or even more when this selection step is completely ignored.

The aim of this article is to prove that the habitual selection of the thermodynamic models is appropriate or not for the primary refining process. For the purpose, two available simulation softwares and thermodynamic models have been analyzed. The research paper focuses on establishing a guide for plant operators with information that has been previously proven, with theoretical support.

In particular, for the oil crude atmospheric distillation (Topping), engineers use almost by default the Peng–Robinson thermodynamic package in Aspen Hysys simulator and Chao–Seader in Aspen Plus. Although the use of the thermodynamic property packages involves a whole theoretical support, this is not considered at the time of their election.

*Keywords* - Crude oil, Distillation, Simulation, Thermodynamic Properties, Topping.

### I. INTRODUCTION

A simulation procedure can be defined as the virtual representation of a process through a mathematical model that describes a physical – chemical phenomenon. This recreation allows obtaining information of the process behavior in different scenarios. The technique has become essential for the accurate execution of industrial plants design, its optimization and operation. An engineer can quickly define a complex flowsheet and all of the process conditions [1].

A process simulator is an instrument that offers the numerical solution of a mathematical model, which includes elements such as [2]:

- Components database, which contains the needed values for the calculation of physical properties starting from the thermodynamic models.
- Thermodynamic models section, that offers a wide range of options for the calculation of liquid-vapor (LVE) and liquid-liquid (LLE) equilibriums, enthalpies and other thermodynamic properties.

- Flowsheet section, related with the flows and equipment under analysis.
- Operating units section, for the realization of matter and energy balances in the different units of operation.
- Output Generator section, it returns a whole report of the simulation results.
- Calculus sequence section that controls the calculation sequence and the simulation convergence.

The functionalities are integrated with the aim of making a simulation case a rapid and easy work. The market develops better, more sophisticated and particular applications for the specific cases in processes engineering. These tools help the researches to purpose new alternatives for the solution of the optimization problems.

#### 1.1 THERMODYNAMIC PROPERTIES

The simulation model consists of a group of equations that characterize the operating units behavior in a process. These equations have a

considerable quantity of terms related to physical and thermodynamic properties of the components and the mixtures involved. Therefore, it is indispensable to include in the simulation case a group of equations for the calculation of these properties. The group of variables to specify includes values of temperature, pressure, composition and certain empirical values for each of the components in all of the process streams.

Any of the simulation case performed requires knowing the physicochemical and thermodynamic mixture properties values. This is required for all the components to employ in the process. The values are needed for all of the conditions –composition, pressure and temperature– that can appear in the normal operation of an industrial plant. In the industry, this situation is in fact unlikely to occur due to the dynamism and the big quantity of values studied [2].

A good selection of the techniques will be essential for an accurate analysis of devices and streams presented in this simulation case. It is not enough to have the most sophisticated available simulator in the market, if a wrong method choice is done, in that case, wrong or imprecise results will be ever obtained.

Evidently, it is impossible to evaluate what package is necessary for all of potential component mixtures performing in a simulation. The only solution is to face the question in a general way, establishing a criteria selection, with an acceptable range of application.

Thermodynamic properties of any component depend on the nature of its molecules. Therefore, in order to make a generalization of fluids properties, a whole comprehension of the molecules behavior is required. Unfortunately, this comprehension is not in hand yet. Available theoretical sources for the estimation of the properties are of rational type -based on thermodynamic laws and molecular behavior kinetic theory-, empirical type -based on the correlation of experimental data for mathematical media-, and mixed type, or the combination of both mentioned classes. Completely empirical correlations are often very useful but its use has to be avoided outside the variables range considered for its deduction. Generally, the reliability of a correlation relies upon how solid is its theoretical basis, particularly when the correlation has been extensively proved with experimental data. However, when the theoretical base is not solid, it is recommendable to base the estimations in experimental data.

## II. ANALYSIS OF THE AVAILABLE MODELS

AspenTech is a provider of smart manufacturing and supply chain management software and services for the process industries. Their simulation products use the concept of ‘Thermodynamic Package’ or ‘Fluid Package’ (FP) as the content of the information required for the calculation of physical, thermodynamic and transportation properties. A FP allows users to organize all the information (properties, components, hypothetical components, interaction parameters, reaction, tabled data, etc.) into a simple internal file. A package consists of a thermodynamic model for the properties calculation, especially for the liquid-vapor equilibrium (LVE). Three advantages can be listed as the consequence of the use of a package:

- All the information associated is defined as a block, which allows the easy creation and modification of the needed data.
- The FP can be stored as a full file to be used at more than one simulation case.
- Several FP can be used in the same simulation case. And all of them can be found into the administrator of the simulators.

AspenTech offers two of the more relevant simulators of processes available in the market for the chemical industry. These simulators are Aspen Plus y Aspen Hysys. Each of them recommends the more appropriate method for a process in particular [1]. This information can be reached by consulting the support section of each of the software. For accessing to this support, the ‘Assistant - Property Method Selection’ (APMS) option is available in both simulators. The precise way for accessing to this section will be described later in this article [3][4].

## III. RECOMMENDED MODELS FOR THE PRIMARY DISTILLATION PROCESS

When a thermodynamic option is selected, the model and other associated models are used for the calculation of thermodynamic and transport properties. These last are needed to develop the simulation case. In the oil industry, the equations of state (EOS) have played a central role in the thermodynamic modeling of vapor-liquid equilibrium (LVE) of hydrocarbons (HC). Nevertheless, EOSs tend to offer inaccurate results under certain conditions.

For these cases, special thermodynamic models may be used. In all of the cases, Aspen Plus y Hysys simulators offer the needed support in order to choose the best thermodynamic package for each case. This support guide is executed by means of their respective assistants.

For petrochemical, oil and gas applications, particularly an oil crude primary distillation (Topping), the Aspen Hysys Assistant – Property Method Selection (APMS) – recommends the selection of the thermodynamic package based on the Peng-Robinson (PR) EOS.

In order to access to the Assistant, a new Hysys case is opened and, then, a thermodynamic package should be added, using the ‘Add’ button, situated in the ‘Simulation Basis Manager’ window, ‘Fluid Pkgs’ flange. Then a new window appears, in this new window localize the ‘Launch Property Wizard’ button. Then, the next steps are chosen, ‘Process type’, ‘Refining’, Crude Tower’ and, finally, ‘Property package description’, as shown in Fig. 1 – 5.

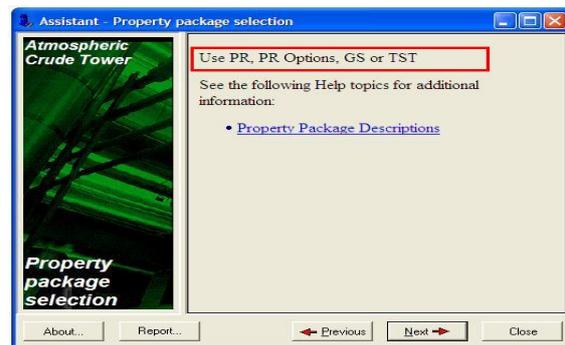
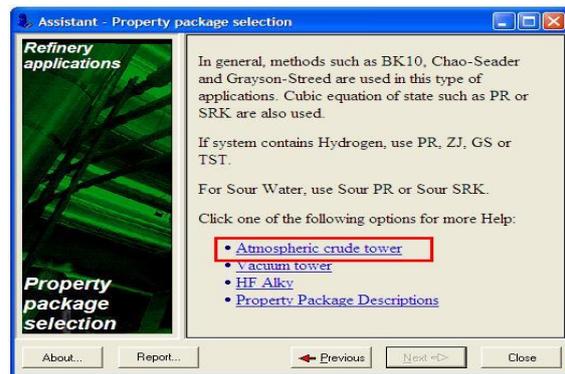
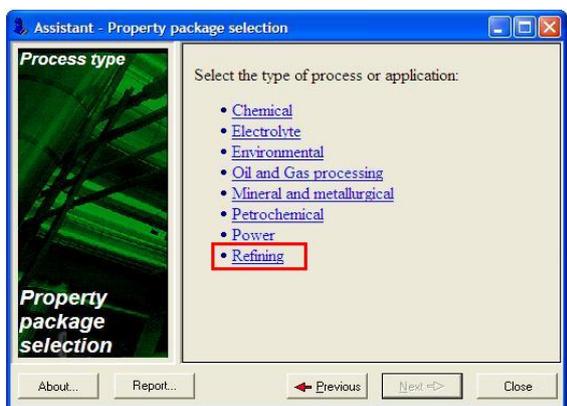
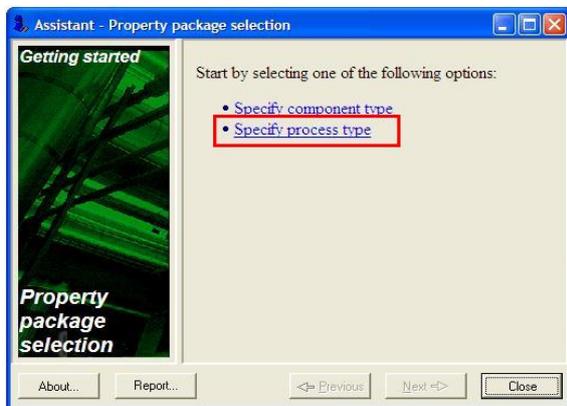
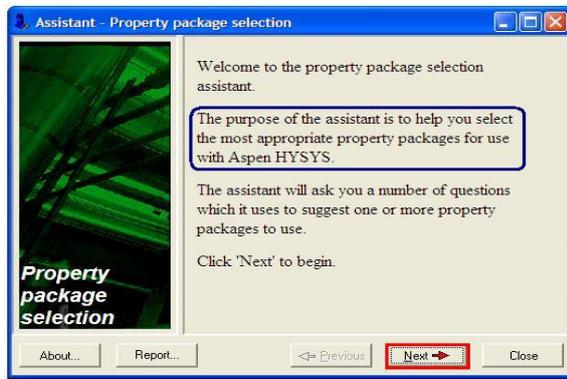


Fig. 1–5: Required steps for accessing to the Aspen Hysys V 7.2 recommended packages.

Aspen Plus recommends thermodynamic packages, designed for HC and light gases, including models for the LVE and liquid fugacity correlations, which are used for medium and low operating pressures. The ‘Petroleum tuned’ EOS are used for high values of pressure. Where possible, density and transport property values are calculated based on the procedure of API (American Petroleum Institute).

Aspen Plus offers a wide database which includes data, particularly distillation curves (Assay), taking as reference characteristic crudes from different oil fields in the world. For example, Labuan and Miri (Malaysia).

Natural gas and oil cuts are composed mainly for hydrocarbons. These complex mixtures are treated as ‘pseudocomponents’. Generally, the thermodynamic models are used for crude oil refining applications. In the particular case of primary refining, Aspen Plus recommends the Chao-Sea (CS) thermodynamic package.

To access to the assistant in Aspen Plus simulator, a new simulation case may be created, a ‘blank simulation’. In the menu bar, ‘tools’ option is chosen. Then, choose ‘Property method selection assistant...’. After that, choose the options ‘Process Type’, ‘Refining’ and, finally, ‘Atmospheric crude tower’. In this last window, the recommended thermodynamic package is shown. More information of each of the packages can be found if its name is selected. See Fig. 6 – 10.

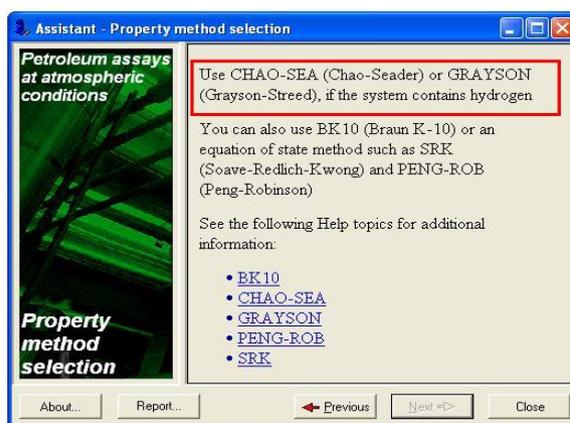
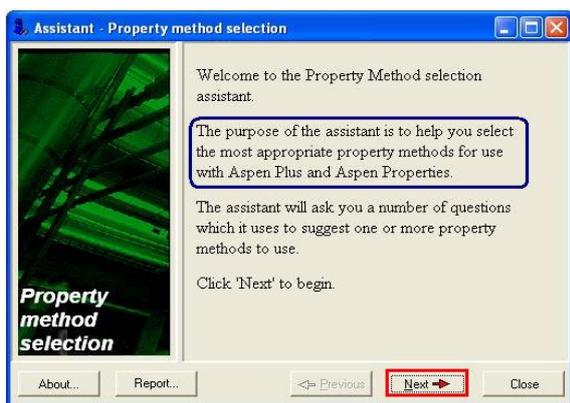
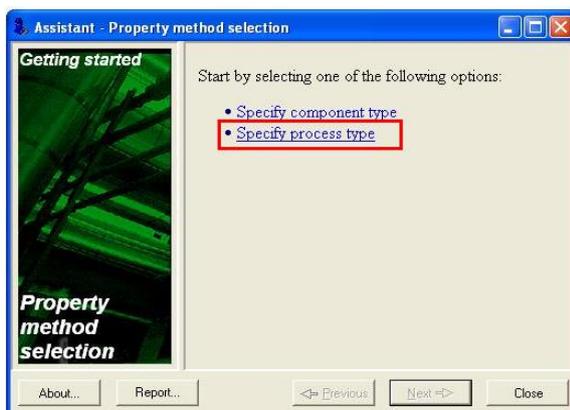


Fig. 6–10: Required steps for accessing to the Aspen Plus V 7.2 recommended packages.



### 3.1 PENG-ROBINSON ANALYSIS

The Peng–Robinson general equation corresponds to a Redlich–Kwong EOS modification, in order to have a more accurate approximation to the VLE state. The PR EOS is represented in Equations 1–4.

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \quad (1)$$

Where:

$$a = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha \quad (2)$$

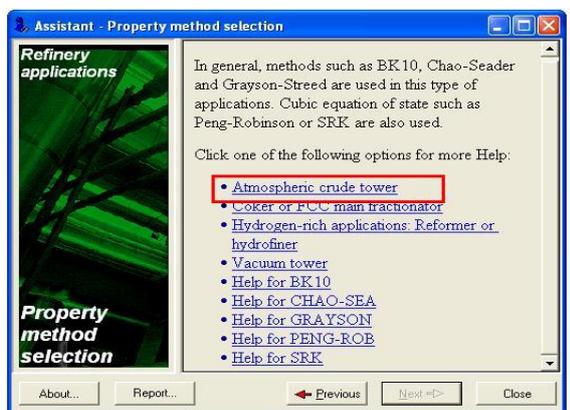
$$\alpha^{0.5} = 1 + \kappa(1 - T_r^{0.5}) \quad (3)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.2699\omega^2 \quad (4)$$

Originally, equations 1–4 were developed for pure components. Therefore, in order to apply them to mixtures, for example oil cuts, it is necessary to adopt the concept of ‘mixing rules’, required in the ‘a’ and ‘b’ terms of Equation 1. Oil cuts are complex mixtures of industrial interest [5].

Mixing rules consist of a group of equations used for the adaptation of the original PR EOS for pure components. The ‘a’ and ‘b’ parameters of the original PR equation are available in bibliography for mixtures. The tutorial section offers a whole list about how to proceed in each case with the mixing rules.

Aspen Hysys includes improvements to the original PR with the aim of extending the applicability range and improve the no-ideal system description. It incorporates a wider range of temperature and pressure, starting with cryogenic to high temperatures; and from vacuum pressures to high pressure systems. It offers a complete database for the binary interaction parameter, implying good results for hydrocarbon mixtures. The same EOS predicts the distribution of heavy petroleum components, aqueous glycol and methanol systems.



For petrochemical or gas and oil applications, the PR EOS is generally the recommended property package. This EOS can be accurate for a wide range of system conditions. It solves rigorously any single, two-phase or three-phase system with a high degree of efficiency and reliability.

### 3.2 CHAO-SEA ANALYSIS

CS package uses the CS-RK method for the LVE calculation and the Lee Kesler method for the calculation of Enthalpy and Entropy. Fugacity coefficients in the vapor phase are calculated by means of the 'corresponding-states principle'. Special functions are incorporated for the calculation of fugacity values in the liquid phase. In Aspen Plus simulator, Chao-Sea thermodynamic package uses:

- The Chao-Seader correlation for the activity coefficient in the reference state.
- Scatchard-Hildebrand model for the activity coefficient.
- Redlich - Kwong equation of state for the vapor phase properties.
- Equation of state for the liquid and vapor enthalpies.
- API method for the molar liquid volume, viscosity and surface tension.

Chao-Seader thermodynamic package must be used for heavy hydrocarbons, with pressure lower than 10342 kPa (1500 psia), and a temperature range of -17.78 to 260°C (0 to 500 F). It is used for vapor systems. Also, it can be used for three phase flashes but restricted to the use of pure water in the second liquid phase. For example, it is recommended to use the CS for cases in which water vapor or liquid are the main components. This is because the package includes specific correlations that represent the vapor tables in a precise way.

The Chao-Sea thermodynamic package is predictive and is developed for hydrocarbon mixtures with light gases (CO<sub>2</sub> or SH<sub>2</sub>). It can be used for crude towers, vacuum towers and ethylene process parts. This model is semi empirical, based on a wide source of hydrocarbon data.

## IV. CONCLUSION

Aspen Hysys simulator uses the PR equation, which is modified following the 'mixing rules', valid for complex systems as oil crude and their cuts. Generally, the more solid is the theoretical base of a correlation, the more reliable it results. Particularly speaking, this correlation was widely proved and, their results were compared with those obtained in real cases of the oil crude primary distillation process.

Aspen Plus uses the Chao-Sea model. Although the theoretical base is not solid, this

simulator compensates it with their wide crude database from all around the world. Its application has to be avoided for outside its valid range. Aspen Tutorial recommends the use of the CS model because its application is reliable thanks to their wide source of information.

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## NOMENCLATURE

FP	Fluid Package
APMS	Assistant - Property Method Selection
EOS	Equation of State
RK	Redlich – Kwong
PR	Peng – Robinson
LLE	Liquid – liquid equilibrium
CS	Chao – Seader
LVE	Vapor – liquid equilibrium
HC	Hydrocarbons
API	American Petroleum Institute
P	Pressure
R	Ideal gas constant
V	Volumen
<i>a</i>	Function
<i>b</i>	Constant
$\alpha$	Function
$\kappa$	Symmetric binary interaction parameter
$\omega$	Acentric factor
$T_C$	Critic Temperature
$P_C$	Critic Pressure
$T_r$	Reference