

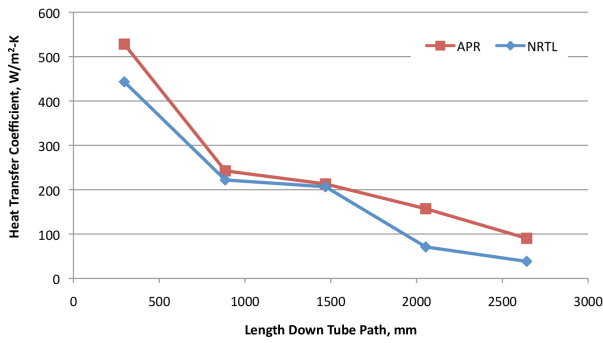
**Patrick S. Redmill, Heat Transfer Research, Inc., USA,** examines how, as heat exchanger calculations become more rigorous, the attraction to greater physical property accuracy grows stronger.

# ATTRACTED TO THE PHYSICAL

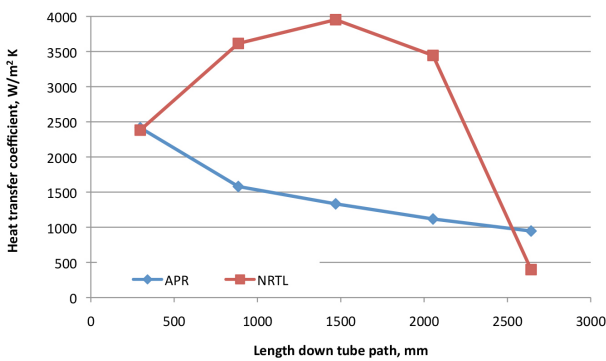
**L**ike many industrial calculations, early heat exchanger rating and design calculations required relatively limited amounts of physical property information, which was easily gleaned from the field or through open literature. As heat exchanger calculations have become more rigorous, the need for greater physical property accuracy has increased. Without accurate physical property estimates, the improvements of rigorous heat exchanger calculations may be lost.

To get estimates for physical properties that were difficult to measure in the field, heat exchanger modellers have to turn to a combination of vapour-liquid equilibria (VLE) calculations and vapour and liquid phase mixing rules. In this article, the combination of VLE and phase mixing rules will be called 'physical property generators'.

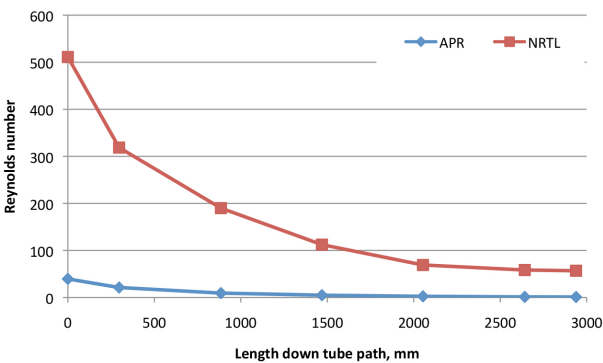
More and more, computational heat exchanger modelling is the first step in the process of designing, fabricating, and installing a heat exchanger. The fluids of interest to be processed in these heat exchangers now go well beyond simple hydrocarbon mixtures. Unfortunately, the mindset around the selection of physical property generators for heat exchanger calculations has not, in the large part, evolved past a small group of long held industrial physical property generator standards. Often, widely used physical property generators feature parameterisation that was established decades ago and are capable of considering only simple, non-polar systems with simple liquid and gas phase mixing behaviours. Notably, physical property calculations without insight on the overall phase behaviour can, and will, generate faulty results for mixtures near the critical point.



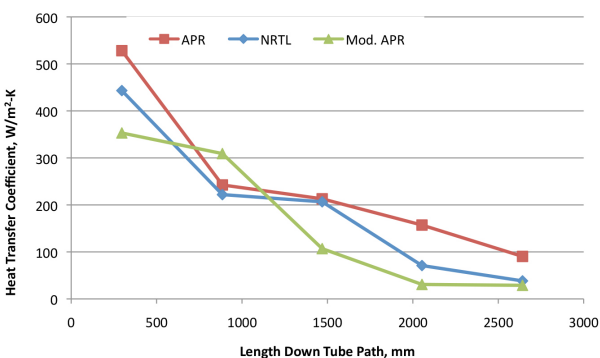
**Figure 1.** Heat transfer coefficients: APR versus NRTL.



**Figure 2.** Convective heat transfer coefficients: APR versus NRTL.



**Figure 3.** Liquid Reynolds numbers: APR versus NRTL.



**Figure 4.** Heat transfer coefficients: APR versus NRTL versus modified APR.

Fortunately, there are many physical property generators that are capable of estimating properties for complex, polar fluids with sophisticated phase mixing rules. This article discusses the capabilities of physical property generators that feature sophisticated correlation of complex VLE, and how the resulting capabilities of these physical property generators are germane to heat exchanger calculations. Two very different, ‘out of the box’ cases and a third case with end user modified VLE parameters are also compared.

## VLE modelling

The VLE component, or equation of state (EOS), of a physical property generator is typically responsible for predicting the phases and their respective compositions in a vapour-liquid fluid mixture. An EOS can take a variety of forms, but this discussion is limited to cubic EOS's and activity coefficient models. The Peng-Robinson EOS, shown below, is perhaps the most recognisable simple cubic equation of state used in process design and simulation:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v-b)+b(v-b)}$$

Where  $P$  is the system pressure,  $T$  is the system temperature,  $v$  is the molar volume,  $a(T)$  represents the average attraction energy between molecules, and  $b$  represents the average molecular volume, also known as the co-volume. These terms are defined based on mixing rules, binary interaction parameters, and the fluid composition.

Rearranging the above equation into a polynomial where  $v$  is the independent variable makes this cubic polynomial form apparent. The cubic polynomial is the simplest function that is capable of representing P-v behaviour for both gases and liquid.

An alternative representation of fluid phase behaviour uses activity coefficients. Very much like the number of EOS's available to the engineer, the number of different activity coefficient models is large.

A commonly used activity coefficient model is the NRTL equation:

$$\ln \gamma_i = x_j^2 \left[ \tau_{ji} \left( \frac{G_{ji}}{x_i + x_j G_{ji}} \right)^2 + \frac{\tau_{ij} G_{ij}}{(x_j + x_i G_{ij})^2} \right]$$

Where  $x_i$  is the liquid mole fraction of component  $i$ ,  $\tau_{ij}$  and  $G_{ij}$  are interaction parameters, and  $\gamma_i$  is the activity coefficient of component  $i$ , which is central to calculating the liquid phase fugacity.

The power of the activity coefficient model lies in its ability to estimate the liquid phase fugacity of a given component independent from the gas phase fugacity. Activity coefficient models are particularly useful for liquid phase systems with partially or completely miscible polar constituents. Additionally, activity coefficient models may be applied in VLE applications where the vapour phase is simple to model or a suitable cubic EOS is available for vapour-phase modelling.

Process conditions	Shell side	Tube side
Fluid	High pressure steam	Water/DEA
Flow rate, kg/s	12.0	2.0
Inlet temperature, °C	300.0	100.0
Inlet pressure, kPa	2500.0	101.325

TEMA type	AES
Shell ID, mm	1250.0
Tube OD, mm	31.750
Tube length, mm	3048.0
Tube layout, °	45
Tubecount	573
Tubepasses	1
Baffle type	Single segmental
Number of crosspasses	5

## Heat exchanger modelling

Modern heat exchanger modelling has to consider not only the existence of two phases (e.g., boiling and condensing) but also fine grained details of various flow regimes, as well as their effect on the heat transfer coefficient and pressure drop ( $\Delta P$ ) on the tube or shell side of the equipment. Furthermore, the heat transfer coefficient and  $\Delta P$  themselves are fundamentally linked. As such, a high accuracy calculation requires a detailed integration incorporating the two parameters down the length of the heat exchanger.

The heat transfer coefficient and  $\Delta P$  are, of course, heavily dependent on physical properties, which are often acquired via a physical property generator. Physical properties relevant to heat exchanger calculations are density ( $\rho$ ), viscosity ( $\mu$ ), heat capacity ( $c_p$ ), thermal conductivity ( $k$ ), thermal expansion coefficient ( $\beta$ ), and surface tension ( $\sigma$ ). Note that these properties are all functions of the vapour-liquid equilibrium calculations, which define the phase compositions and the associated physical properties required for the calculation of heat transfer coefficients. Furthermore, the amounts of liquid and vapour define the equipment duty. Depending on the location in the phase diagram, the degree of turbulence, and the boiling/condensation regime (if applicable), the underlying heat transfer and  $\Delta P$  phenomena can be very sensitive to variations in physical property parameters. The physical property generator most appropriate for a given fluid must be carefully considered.

## Understanding the toolbelt

Unfortunately, when modelling complex fluids, no physical property generator offers a 'silver bullet'. Many specialised EOSs apply to complex fluids and processes, such as polar mixtures, amine sweetening,

sulfur recovery, acid/water solutions, etc. However, end users typically need to understand the complexities of the fluid to prescribe the appropriate EOS. At the very least, end users should feel comfortable changing the EOS and/or mixing rules, noting the differences in physical properties, and then rationalising those differences. They may then be motivated to seek experimental data and further validate the calculations.

This study limits the scope to polar systems, which are among the fluids with the least understood molecular interactions. However, polar fluids are also one of the most commonly encountered complex fluids in heat exchanger calculations – think water! Furthermore, physical property generators are often applied, with insufficient correlation, in heat exchanger calculations with complex polar fluids. This practice may produce dubious results. The importance of properly modelling polar fluids in heat exchanger models cannot be undervalued.

While careful consideration should be given to the composition of any system being modelled, systems containing industrially relevant components, such as water, alcohol, amines and glycols, should be regarded as polar. These require physical property generations with polar interaction considerations. Alkane fluid mixtures, which are typically the primary constituent in oil and gas hydrocarbon streams, are generally regarded as non-polar and may be modelled with a wider array of physical property generators that do not feature polar interaction correlations.

## One caveat

In calculations for mixtures containing water and hydrocarbons, it is important to ensure that the thermodynamic model properly represents the vapour-liquid-liquid (VLE) behaviour. Most industrial equations of state used for process design provide support for water-hydrocarbon systems.

## Case study

This example illustrates the importance of properly selecting a physical property generator for polar fluid applications in a heat exchanger.

The fluid is a water/diethanolamine (DEA) solution on the tube side of a shell and tube heat exchanger. For the heat exchanger calculation, **Xist**<sup>®</sup> is used, comparing three sets of results: two use 'out of the box' packages Advanced Peng Robinson (APR) and NRTL physical property generators from Virtual Materials Group, Inc.<sup>3</sup> with mass weighted mixing rules, and a third uses the APR package with a modified  $k_{ij}$  parameter fitted from literature data. The APR package from Virtual Materials Group is the default choice in **Xist**.

The water/DEA fluid enters the tube side of the heat exchanger as a dilute solution with a 0.99/0.01 molar water/DEA concentration. The fluid enters as a saturated liquid and exits the heat exchanger at a mass vapour quality of 80%. More process and heat exchanger details are given in Tables 1 and 2.

## Results

The *Xist* rating calculation using the APR physical property package produces an oversize (OD%) of +13%, whereas the NRTL package produces an OD% of -12%. The OD% is defined as:

$$OD\% = \left( \frac{Q_{prod}}{Q_{req'd}} - 1.0 \right) 100$$

Where  $Q_{prod}$  is the heat duty predicted in the calculation and  $Q_{req'd}$  is the required heat duty of the heat exchanger.

The resulting discrepancy is significant, especially when one considers that many engineering teams would simply send the APR calculation on to design or even fabrication. Conversely, the shell and tube configuration using the NRTL model would likely be dismissed.

A closer look at the final results indicates that  $\Delta P$  is not contributing to the discrepancies in oversize. Both tubeside streams have an innocuous  $\Delta P$  of about 4 kPa, with very similar looking profiles. However, a comparison of the heat transfer coefficients (Figure 1) tells a somewhat different story. The heat transfer coefficient in the NRTL case is significantly lower than that of the APR calculation in the last third of the tube. An inspection of the boiling regimes in each case shows that the APR case is in stratified convective and nucleative boiling. The NRTL calculation, on the other hand, falls into film boiling in this section of tube. The boiling regime is characterised by the calculation of the boiling heat flux exceeding a critical heat flux, at which point the tubeside fluid is blanketed by vapour at the walls of the tube, significantly compromising heat transfer.

So the question remains: what is the connection between the physical properties, as generated by NRTL, and the invocation of the film boiling regime? As mentioned previously, when the flow boiling heat (convective and nucleative) exceeds a critical heat flux, film boiling occurs. Figure 2 shows that the NRTL-calculated convective heat transfer coefficient is much higher than that of APR. This high calculated convective heat transfer coefficient pushes the flow boiling heat flux past the critical value for film boiling.

The differences in the calculated convective heat transfer coefficients are due to the fact that the NRTL case has a significantly higher tubeside liquid Reynolds number, which enhances the convective heat transfer coefficient. The elevated Reynolds number, shown in Figure 3, results from an NRTL-calculated liquid  $\mu$  that is significantly lower than that of the APR calculation. The NRTL liquid  $\mu$  for the dilute DEA/water system at 100°C is between 0.32 - 0.50 cP, which is relatively close to that of pure water. By contrast, the APR-calculated liquid  $\mu$  for the system is between 4.1 - 16.0 cP, up to two orders of magnitude difference from that of pure water.

Conventional wisdom (and experimental measurement)<sup>4</sup> dictates that a dilute aqueous DEA solution should not have a liquid phase viscosity two orders of magnitude more viscous than that of pure water, and that NRTL is likely


giving a more accurate representation of the liquid phase  $\mu$ . A final look at the generated physical properties, for both APR and NRTL, provides an interesting clue. NRTL predicts only a single liquid phase, whereas APR predicts two immiscible phases. Knowing that both molecules are polar and strongly interact favours the conclusions that DEA and water are mutually soluble and produce only a single liquid phase. It is reasonable to hypothesise that the APR package lacks the proper DEA and water interactions and, thus, mischaracterises the liquid phase.

To test this hypothesis, the DEA and water  $k_{ij}$  parameter is fitted from a relevant literature study<sup>5</sup>, the APR default  $k_{ij}$  is replaced with the calculated value ( $k_{ij} = -0.216$ ), and finally regenerate and tabulate the physical properties. This table is then fed to the *Xist* calculation, yielding an OD% of -28%.

Similarly to the NRTL case, the modified APR case predicts a single liquid phase and a liquid  $\mu$  relatively close to that of pure water (0.32 - 0.60 cP). Furthermore, like the NRTL case, the modified case results in the invocation of film boiling and, thus, a negative OD%. Figure 4 shows the heat transfer coefficient profile for the modified APR case relative to the NRTL and APR cases. The differences in bulk liquid  $\mu$  can be attributed, perhaps, to the discrepancy in viscosity mixing rules between single phase and multiple phase liquid systems.

## Conclusion

The choice of a physical property generation package can have a fundamental impact on the perceived viability of a shell and tube heat exchanger design. The case study exhibits a significant change in liquid phase  $\mu$  when the calculation uses two seemingly appropriate physical property generators. This shift in  $\mu$  ultimately leads to the invocation of a sub-optimal boiling regime, which significantly and negatively impacts performance.

This exercise illustrates the sensitivity of rigorous heat transfer correlations and the importance of good physical property generation. With a rudimentary understanding of the underlying chemistry of a given system and the capabilities of commercially available physical property generators, end users can make informed physical property generator choices. Increased understanding of physical property generator capabilities is likely to lead to better heat exchanger designs, which, in turn, will result in optimised equipment in the field. 

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