Online Chemical
Engineering Information

Modeling Urea Processes: A New Thermodynamic Model and Software Integration Paradigm

Introduction

Nitrogen based fertilizers are the most widely produced types of fertilizers, accounting for 82.79 million tones produced worldwide between 1998 and 1999 (1). Amongst all nitrogen based fertilizers urea is the most widely produced, with 37.57 million tones produced between 1997 and 1998 (1). It is significant to notice that urea consumption is increasing significantly, jumping from 8.3 million tones in 1973-1974 to 37.57 million tones in 1997-1998 corresponding to about 46% of the total world consumption of nitrogen. The importance of urea production and the availability of modern flowsheeting tools motivated us to apply basic thermodynamic principles and software engineering for the creation of a tool that can be used for modeling the most significant aspects of the urea production processes currently used. Albeit several technologies are available for the production of urea (2, 3, 4, 5, 6), the Stamicarbon and Snamprogetti processes correspond to approximately 76% of the world market (7) and therefore our modeling efforts concentrated on these two production technologies. Basic Principles The commercial production of urea is based on the reaction of ammonia and carbon dioxide at high pressure and temperature to form ammonium carbamate, which in turn is dehydrated into urea and water:

$$2NH_3 + CO_2 \rightarrow NH_2COONH_4 \quad (1)$$

$$NH_2COONH_4 \Leftrightarrow NH_2CONH_2 + H_2O \quad (2)$$

Reaction 1 is fast, highly exothermic, and goes essentially to completion under normal industrial processing conditions, while reaction 2 is slow, endothermic and usually does not reach thermodynamic equilibrium under processing conditions. It is common practice to report conversions in a CO_2 basis. According to Le Chatellier's principles, the conversion increases with an increasing NH_3/CO_2 ratio and temperature, and decreases with an increasing H_2O/CO_2 ratio.

Different urea production technologies basically differ on how urea is separated from the reactants and how ammonia and carbon dioxide are recycled. Refinements in the production technology usually are concentrated in increasing carbon dioxide conversion, optimization of heat recovery and utility consumption reduction.

Stamicarbon Process (Carbon Dioxide Stripping)

"NH_3 and CO_2 are converted to urea via ammonium carbamate at a pressure of approximately 140 bar and a temperature of 180-185° C. The molar NH_3/CO_2 ratio applied in the reactor is 2.95. This results in a CO_2 conversion of about 60% and an NH_3 conversion of 41%. The reactor effluent, containing unconverted NH_3 and CO_2 is subjected to a stripping operation at essentially reactor pressure, using CO_2 as stripping agent. The stripped-off NH_3 and CO_2 are then partially condensed and recycled to the reactor. The heat evolving from this condensation is utilized to produce 4.5 bar steam, some of which can be used for heating purposes in the downstream sections of the plant. Surplus 4.5 bar steam is sent to the turbine of the CO_2 compressor.

The NH_3 and CO_2 in the stripper effluent are vaporized in a 4 bar decomposition stage and subsequently condensed to form a carbamate solution, which is recycled to the 140 bar synthesis section. Further concentration of the urea solution leaving the 4 bar decomposition stage takes place in the evaporation section, where a 99.7% urea melt is produced." (6)

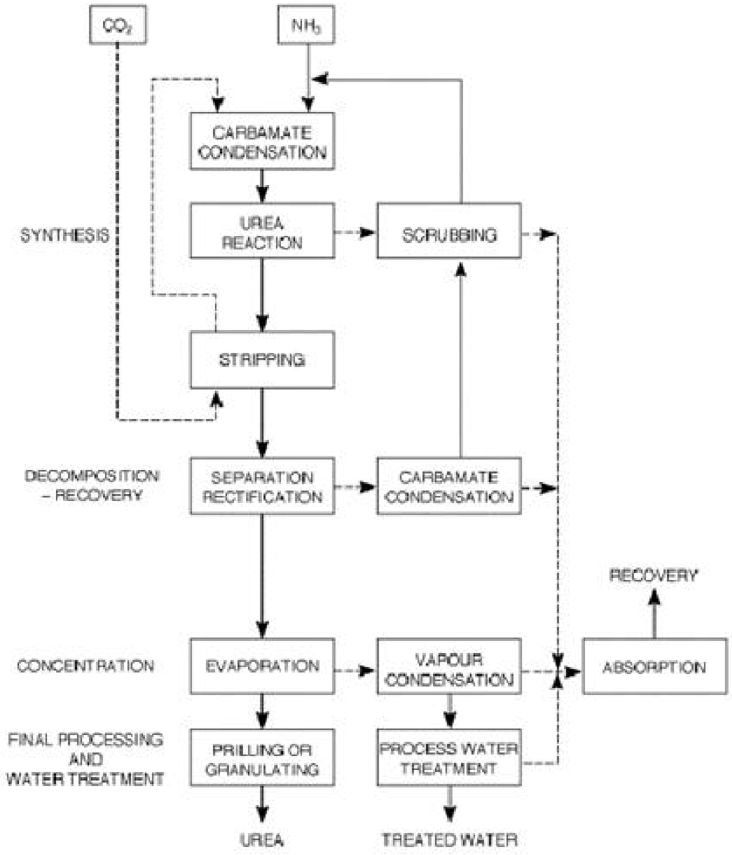


Figure 1: Total Recycle CO2 Stripping Urea Process (6)

Snamprogetti Process (Ammonia Stripping)

"NH_3 and CO_2 are converted to urea via ammonium carbamate at a pressure of 150 bar and a temperature of 180° C. A molar ratio of 3.5 is used in the reactor giving a CO_2 conversion of 65%. The reactor effluent enters the stripper where a large part of the unconverted carbamate is decomposed by the stripping action of the excess NH_3. Residual carbamate and CO_2 are recovered downstream of the stripper in two successive stages operating at 17 and 3.5 bar respectively. NH_3 and CO_2 vapors from the stripper top are mixed with the recovered carbamate solution from the High Pressure (HP)/Low Pressure (LP) sections, condensed in the HP carbamate condenser and fed to the reactor. The heat of condensation is used to produce LP steam. The urea solution leaving the LP decomposition stage is concentrated in the evaporation section to a urea melt." (6)

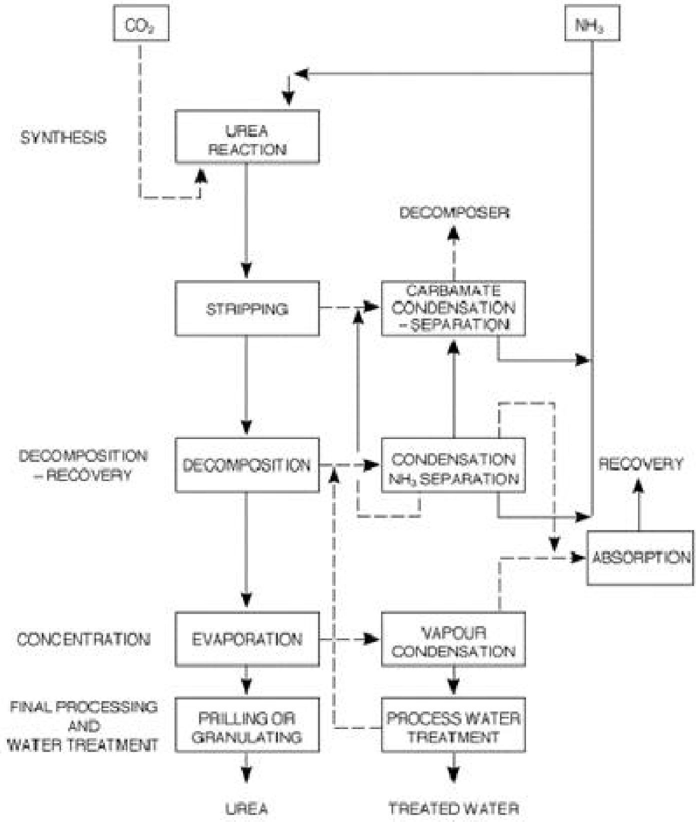


Figure 2: Total Recycle NH3 Stripping Urea Process (6)

Thermodynamic Modeling

Urea processes are challenging to model from a thermodynamic point of view. From one side, accurate low pressure equilibrium thermodynamic equilibrium is necessary to model aqueous urea solutions, while accurate high pressure modeling is necessary to properly model the high pressure synthesis reactor. The thermodynamic package also has to properly take into account the formation of new chemical species, some which are ionic. The effect of minute amounts of inerts in the saturation bubble pressure also has to be taken into account. In addition, the model has to provide reasonable enthalpy and entropy values for flowsheeting calculations. Last but not the least, some operations in the urea process require special behavior from the property package calculation engine and proper communication between the unit operations and the property package system has to be implemented.

The thermodynamic modeling is conveniently divided into high pressure and medium / low pressure areas. In the high-pressure section we have a non-aqueous ionic system while in the medium / low pressure areas we have an aqueous ionic system.

High Pressure Equilibrium

Initially the high-pressure section was modeled using a full ionic model as described by Satyro (8). Albeit the model showed good performance when used to model industrial units, enhancements were possible in terms of computational speed and accuracy with respect to ammonia and carbon dioxide vapor compositions at the outlet of the urea synthesis reactor. The majority of the time spent in thermodynamic calculations was determined to be in the convergence of the ionic chemical equilibrium, and any simplification in that area would have significant impact in the calculation speed, and therefore would allow the use of the model not only for steady state calculations but also dynamic calculations necessary for safety studies and operator training.

The reactive system was simplified by considering all the chemical species in their molecular states. This is not true from a purely physical-chemical point of view, since the reactions happening in the liquid phase at high pressure are well represented by the following reaction system (8):

$$CO_2(l) + 2NH_3(l) \Leftrightarrow H_2NCOO^-(l) + NH_4^+(l) \qquad (3)$$

$$CO_2(l) + NH_3(l) + H_2O(l) \Leftrightarrow HCO_3^-(l) + NH_4^+(l) \qquad (4)$$

$$CO_2(l) + NH_3(l) \Leftrightarrow H_2NCOOH(l) \qquad (5)$$

$$H_2NCOO^-(l) + NH_4^+(l) \Leftrightarrow H_2NCONH_2(l) + H_2O(l) \qquad (6)$$

$$2NH_2CONH_2(l) \Leftrightarrow NH_3(l) + NH_2CONHCONH_2(l) \qquad (7)$$

The equilibrium constants for the equations above are functions of temperature, and the reaction equilibrium is supposed to be independent of pressure. Therefore, the equilibrium compositions for the several species (molecular and ionic) can be represented as in Equation 8:

$$K_i(T) = K_i^x(x)K_i^\gamma(T,x) \tag{8}$$

Where the index i represents one of the chemical reactions defined by Equations 1 to 4, x is the composition vector in the liquid phase, T is the liquid phase temperature and the K's on the right of Equation 5 are defined as in Equations 9a and 9b.

$$K_i^x = \frac{\left(\prod_{j=1} x_j^{v_j}\right)_{Products}}{\left(\prod_{k=1} x_k^{v_k}\right)_{Reactants}} \tag{9a}$$

$$K_i^\gamma = \frac{\left(\prod_{j=1} \gamma_j^{v_j}\right)_{Products}}{\left(\prod_{k=1} \gamma_k^{v_{kj}}\right)_{Reactants}} \tag{9b}$$

Where γ is the activity coefficient and v is the stoichiometric coefficient for each of the components present in reaction i.

The calculation of ionic species activity coefficients is somewhat laborious and the details can be found in Satyro (8). Since the chemical equilibrium has to be evaluated at every iteration when calculating liquid phase fugacity coefficients, any reduction in computational load while keeping accuracy will translate into substantial time saving. Therefore, the reaction system defined by Equations 3 to 7 was replaced by the following simplified system:

$$2NH_3 + CO_2 \Leftrightarrow NH_4COONH_2 \tag{10}$$

$$NH_4COONH_2 \Leftrightarrow NH_2CONH_2 + H_2O \tag{11}$$

$$NH_3 + CO_2 + H_2O \Leftrightarrow NH_4HCO_3 \tag{12}$$

At equilibrium, the actual composition of the liquid phase will be denoted by z and the equilibrium expression is then given by:

$$\phi_i^v y_i P = \gamma_i z_i f_i^o \tag{13}$$

For convenience we note that the fugacity coefficient in the liquid phase is given by the following:

$$\phi_i^l = \frac{\gamma_i z_i f_i^o}{x_i P} \tag{14}$$

Note that even if the solution was ideal from a physical point of view the fugacity coefficient is not unitary unless chemical reactions are not present. This is caused by the fact that the ratio z_i / x_i will be unitary only and only if the liquid phase does not present chemical reactions. The salts present in solution, ammonium carbamate, urea and ammonium bicarbonate are not present in the vapor phase and therefore have infinitesimal volatility.

Careful analysis of the performance of different activity coefficient models on the representation of ammonia and water vapor-liquid equilibrium determined the final model used in this study and a 4 suffix Margules expression was determined optimal for our purposes as defined in the equations below:

$$\ln \gamma_i = (1 - x_i)^2 \left[A_i + 2x_i (B_i - A_i - D_i) + 3D_i x_i^2 \right] \tag{15}$$

$$A_i = \frac{1}{(1 - x_i)} \sum_{j=1}^{nc} x_j a_{ij} \tag{16}$$

$$B_i = \frac{1}{(1 - x_i)} \sum_{j=1}^{nc} x_j a_{ji} \tag{17}$$

$$D_i = \frac{1}{(1 - x_i)} \sum_{j=1}^{nc} x_j d_{ij} \tag{18}$$

Where d_{ij} is a symmetric, temperature independent interaction parameter and a_{ij} is defined as:

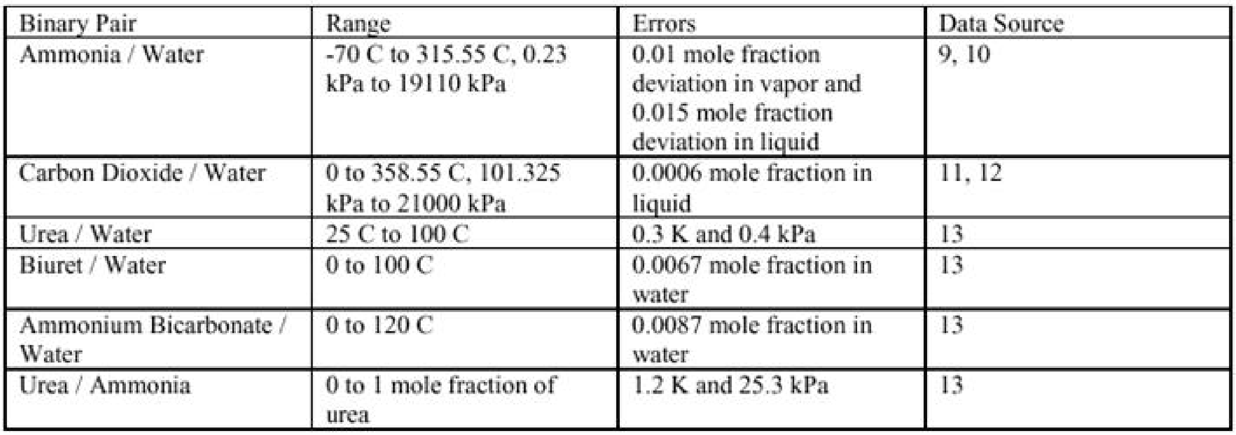
$$a_{ij} = a'_{ij} + \frac{b'_{ij}}{T} + c'_{ij} \ln T \tag{19}$$

Standard state fugacities are determined based on vapor pressures for most components while specially determined standard state fugacities for ammonia and carbon dioxide are used, which are valid from 200 to 500 K.

High Pressure Data Regression

Binary interaction parameters were determined for the following binary pairs based on published experimental data as described in Table 1.

Table 1: Binaries and Ranges for Urea Modeling



Binary Pair	Range	Errors	Data Source
Ammonia / Water	-70 C to 315.55 C, 0.23 kPa to 19110 kPa	0.01 mole fraction deviation in vapor and 0.015 mole fraction deviation in liquid	9, 10
Carbon Dioxide / Water	0 to 358.55 C, 101.325 kPa to 21000 kPa	0.0006 mole fraction in liquid	11, 12
Urea / Water	25 C to 100 C	0.3 K and 0.4 kPa	13
Biuret / Water	0 to 100 C	0.0067 mole fraction in water	13
Ammonium Bicarbonate / Water	0 to 120 C	0.0087 mole fraction in water	13
Urea / Ammonia	0 to 1 mole fraction of urea	1.2 K and 25.3 kPa	13

Typical results for ammonia/water, urea/water, and urea/ammonia are presented in Figures 3, 4, and 5.

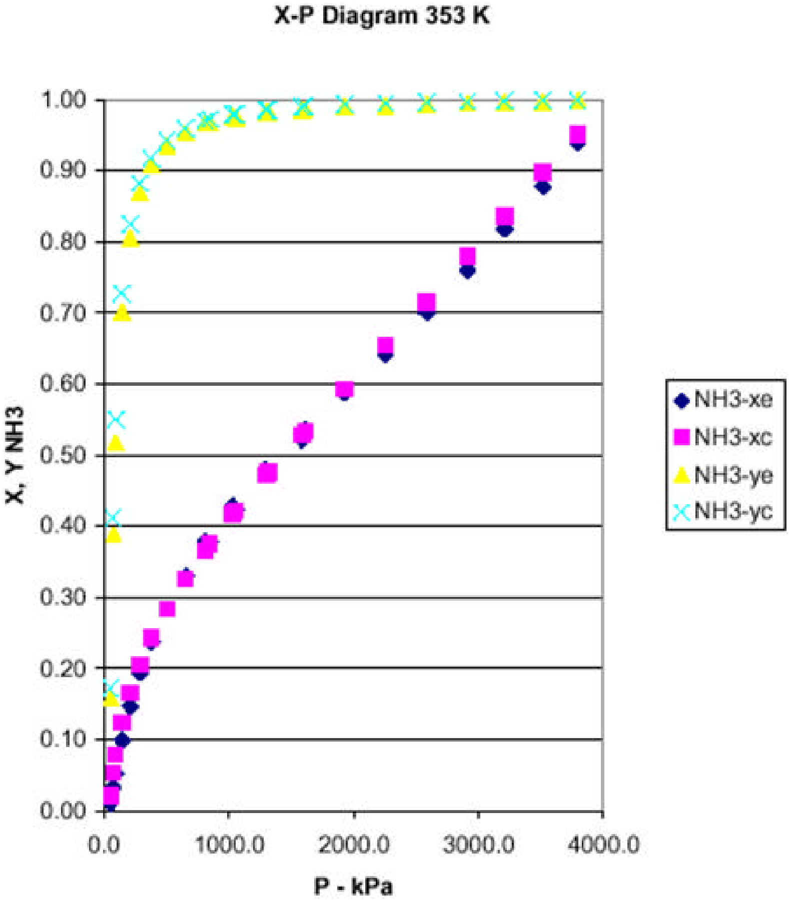


Figure 3: Ammonia Water Vapor-Liquid Equilibrium at 80 °C

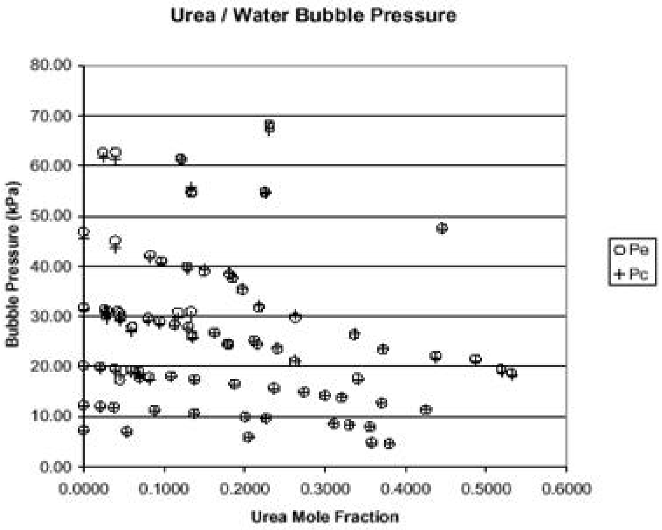


Figure 4: Urea/Water Bubble Pressures

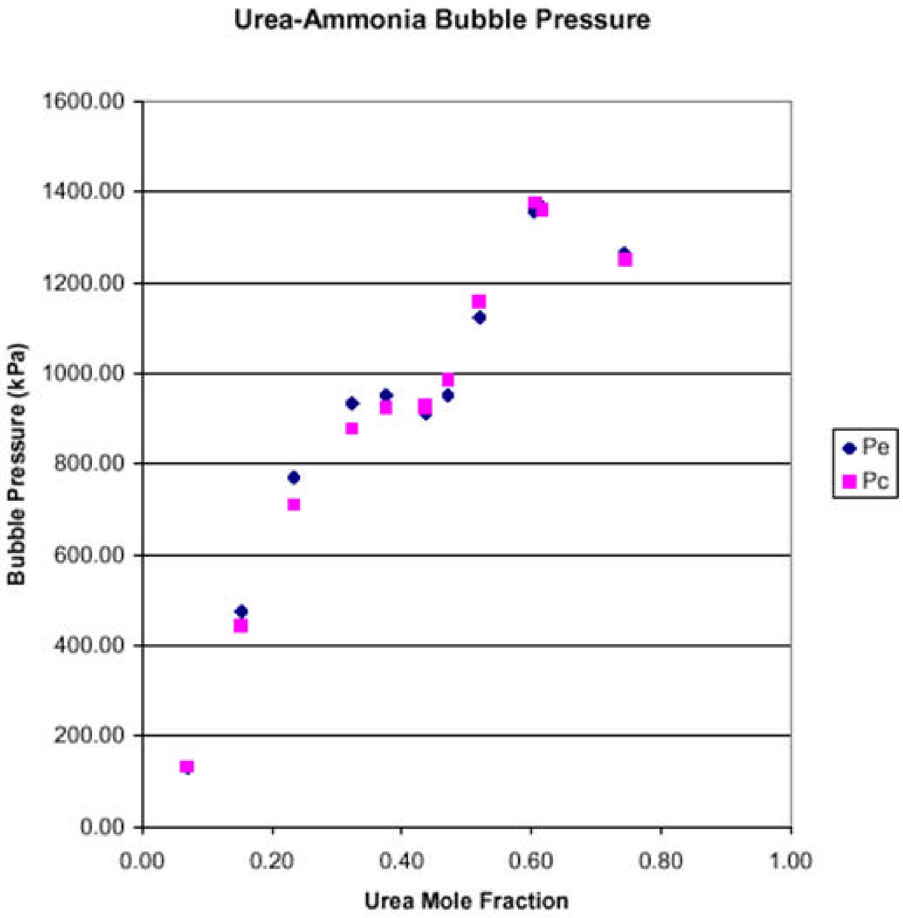


Figure 5: Urea/Ammonia Bubble Pressures

The interaction parameters for the binaries defining the partial pressures of carbon dioxide and ammonia at high pressures were determined based on data published by Lemkowitz and co-workers (14, 15, and 16). The results show an actually better performance than the previous ionic model as shown in the isotherms at 150, 180 and 200° C. The experimental points for each isotherm were determined by constructing Clapeyron plots for each isoconcentrations published by Lemkowitz and then determining the bubble pressure for each isotherm.

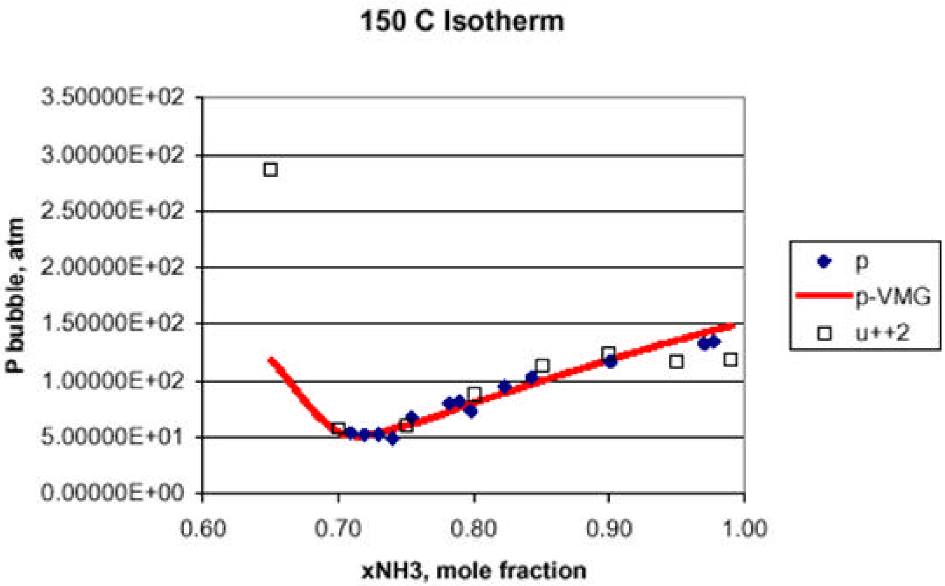


Figure 6: Reactive Isotherm at 150 °C. Red line is molecular model, open squares UREA++ 2.0 using ionic model

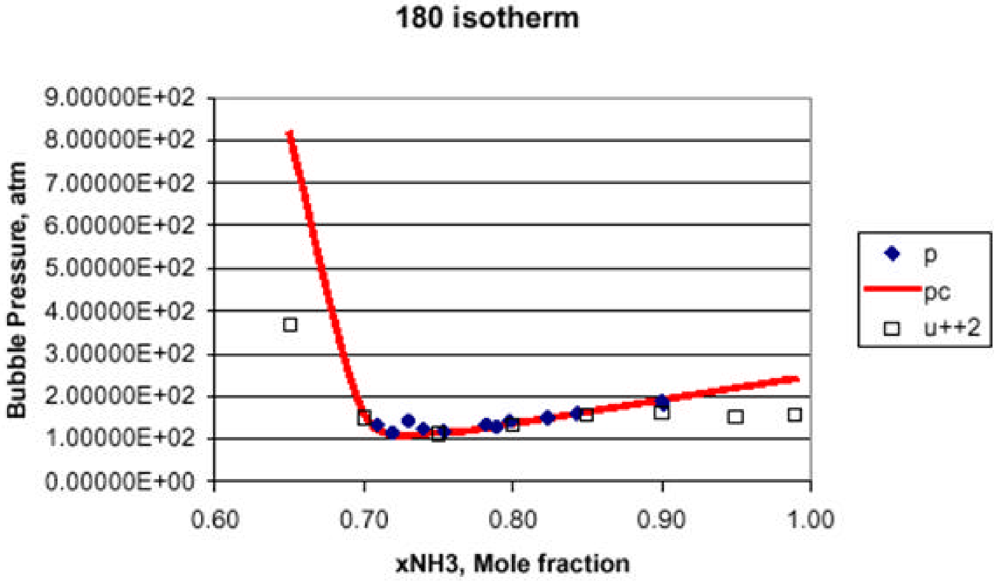


Figure 7: Reactive Isotherm at 180 °C. Red line is molecular model, open squares UREA++ 2.0 using ionic model

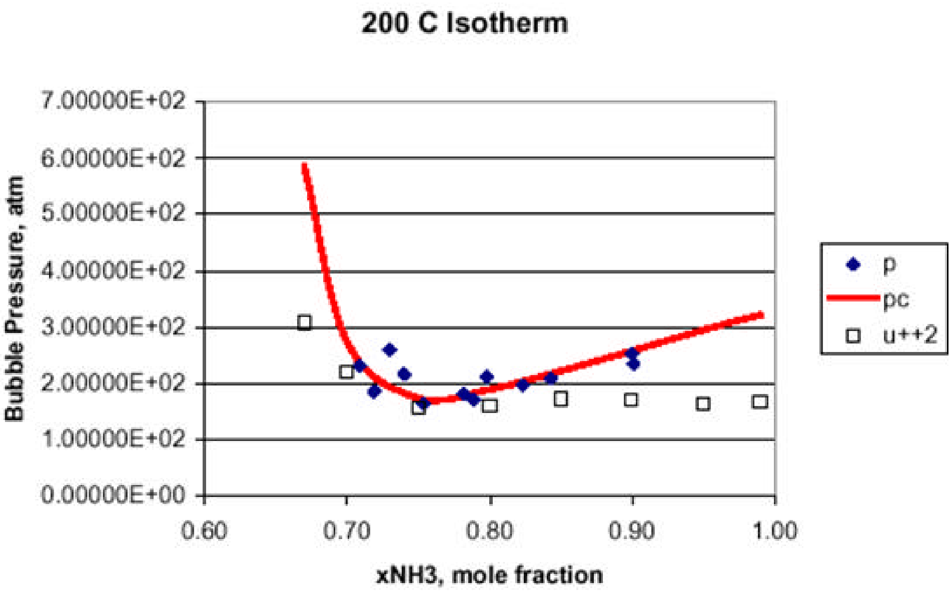


Figure 8: Reactive Isotherm at 200 °C. Red line is molecular model, open squares UREA++ 2.0 using ionic model

Low and Medium Pressure Equilibrium

At low and medium pressures the mixtures are mostly concentrated solutions of water and urea with dissolved carbon dioxide and ammonia. A considerable body of work exists for sour water systems without dissolved urea (17, 18, 19, and 20). In this work, the model proposed by Edwards and co-workers (18) is used with specially determined interaction parameters between ammonia / urea and carbon dioxide / urea to properly account the presence of urea in the solution (21).

Equilibrium Reactor Modeling

A useful tool for mass and energy balances in a urea plant is an equilibrium reactor, which can be used to estimate the performance of actual reactors at optimum conditions (from a thermodynamic point of view). Which can be used as a first approximation for the synthesis reactor. Usually reactors with more than nine baffles approach the results one would get by assuming complete chemical equilibrium as reported by Uchino (5). Also, equilibrium reactors provide a convenient tool for initial studies on how water will affect the reactor performance and can replace empirical graphical relationships used in hand calculations (22, 23). For the we use the ionic reaction system defined by reactions 3-7. Comparisons between predicted and calculated results can be found in Figure 9.

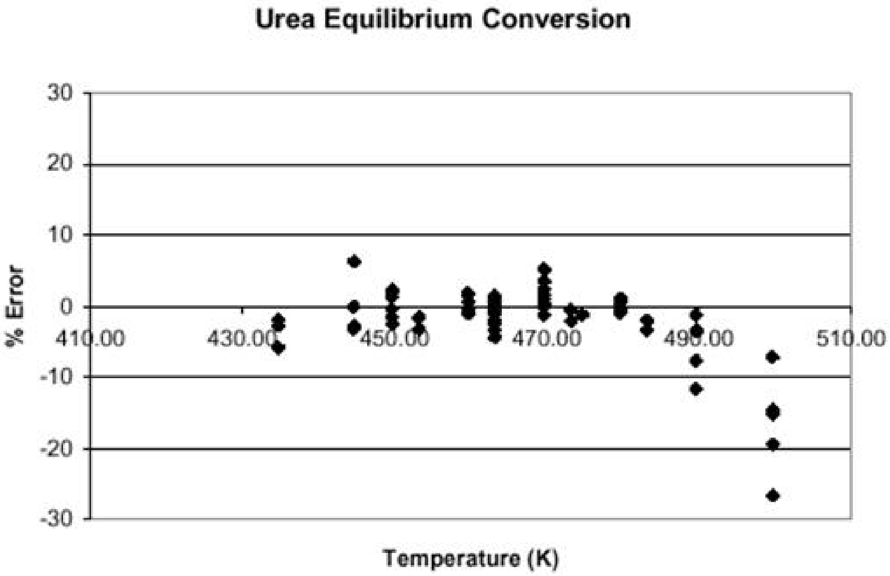


Figure 9: Error in Predicting CO2 Conversion for Urea Equilibrium Reactor (24)

Modeling of specific urea processing unit operations

Several of the unit operations found in the urea process are not found in process simulators, and some ingenuity is required for their proper modeling. This section describes some of these unit operations and the steps taken for their modeling. The discussion is based on the Stamicarbon process.

Urea Synthesis Kinetic Reactor Model

Before the urea synthesis reactor model can be used for predictions, it needs to be tuned. There are two major parameters that are determined during the tuning process. These are a) determining the amount of ammonium carbamate in the reactor feed and b) the equivalent kinetic reactor volume. In order to do this, reactor performance and feed composition needs to be known for at least one operating point.

Determine the amount of Carbamate in the Feed

The feed composition is known in terms of CO_2 and NH_3 and not in terms of the amount of carbamate present. The first step is to use the UREA++ equilibrium reactor in order to compute the equilibrium carbamate leaving the reactor at the process reactor outlet temperature. In the equilibrium reactor, the urea reaction equilibrium constant efficiency is adjusted such that the actual CO_2 conversion is matched. Then the inlet carbamate content is adjusted (keeping the total amount of CO_2 and ammonia constant) to obtain an adiabatic reactor.

Reactor Kinetic Model

The plate type synthesis reactor can be modeled as a set of equilibrium and reactor stages. Since the Carbamate formation reaction is fast it can be modeled as an equilibrium reaction. The carbamate decomposition into urea is slow and is modeled as a kinetic (CSTR) reaction. The equilibrium constants for the carbamate formation are well known, as are the kinetic parameters for the carbamate decomposition into urea. It is found that for plate type reactors, 3 stages are often enough to model the synthesis reactor. A typical example is shown in Figure 10.

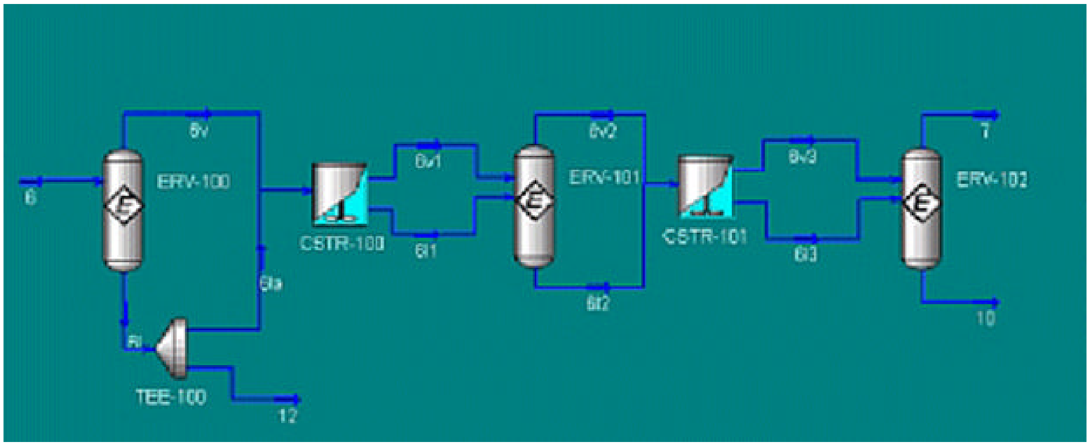


Figure 10: Kinetic Reactor Model

Determine kinetic reactor volume

The kinetic reactor volume of each stage can be adjusted such that the desired urea formation is achieved at the known process conditions. Thereafter the reactor model can be used for predicting the performance due to changing flows and compositions.

High Pressure Stripper Model

The high-pressure stripper is a carbamate decomposer. The high concentration of CO_2 pushes the carbamate decomposition toward completion. This unit-operation is a non-equilibrium process and cannot be modeled using standard equilibrium thermodynamics. The presence of the CO_2 strips the reactor products of its ammonia and CO_2. In addition, any CO_2 and ammonia produced by carbamate decomposition is also stripped by the flowing CO_2. This process seems to be mass transfer controlled, and it is currently modeled by assuming that all the free CO_2, ammonia and all the products of the decomposed carbamate get carried up with the stripping CO_2. Heat balances reveal that about 75% of the energy in the High Pressure Stripper is consumed by the carbamate decomposition and the rest is taken up as sensible heat. A component-splitter unit-operation such as the one provided by the HYSYS process simulator (25) is used to model this non-equilibrium process. Knowing the distribution of the energy for carbamate decomposition and sensible heat it is possible to create a semi-predictive model of the Stripper as steam and process flow changes.

High Pressure Scrubber

The vent from the synthesis reactor is scrubbed in this vessel. Some carbamate is formed and heat has to be removed from the system. There are two components to the removed heat: the sensible heat and the heat of reaction due to carbamate formation. The amount of carbamate formed can be back calculated from the process temperatures and the amount of heat supplied.

High Pressure Condenser

This unit operation supplies the feed to the synthesis reactor. As such the amount of carbamate formed and leaving this condenser is known (see Reactor Tuning). Hence this unit-operation can be modeled as a simple conversion reactor where the CO_2 conversion to ammonium carbamate is known.

Low Pressure Desorbers and Hydrolyzer Model

This part of the flowsheet can be directly modeled using Urea++. No special considerations are required. Predicted are within 0.5 °F of plant performance and predicted compositions are within 1% of plant measurements.

Software Implementation

Process simulation is a tool that shows its power when widely available to process engineers, allowing them to perform better understand the process, propose changes to the process to fine tune performance based on particular characteristics of their plants, markets and economic situation. Therefore, although a rigorous thermodynamic model of the process is a necessary condition for success, it is not sufficient. Some proprietary urea simulation programs exist (7, 26), but they seem to be available only to a handful of users. Our objective was to combine excellence in science with excellence in software to create a solution, which in turn can be used by a wide audience, made up mostly of process engineers, not thermodynamic specialists. Therefore, a robust implementation of the mathematical model would have to be combined with a robust software implementation to allow physical property calculations to be available over a wide range of software platforms (27).

Our choice was to create a central core of classes programmed using the C++ programming language (26). This central core implements all the necessary support functions for the creation of physical property systems, and it is very flexible in terms of physical properties it can handle. Complete support for pure component property configuration, interaction parameter configuration, physical property definition and property package definition (which is nothing more than a collection of physical properties, pure components and interaction parameter matrices) is provided. This allows us to create complete property packages with maximum reuse of parts in an extremely efficient and fast manner.

On top of this core set of classes, software interfaces are implemented allowing our property package system to be used by many diverse applications, ranging from a steady state and dynamic simulator such as HYSYS to batch process simulators, operator training simulators and productivity tools such as Excel, Java and Visual Basic. This functionality is shown schematically in Figure 11.

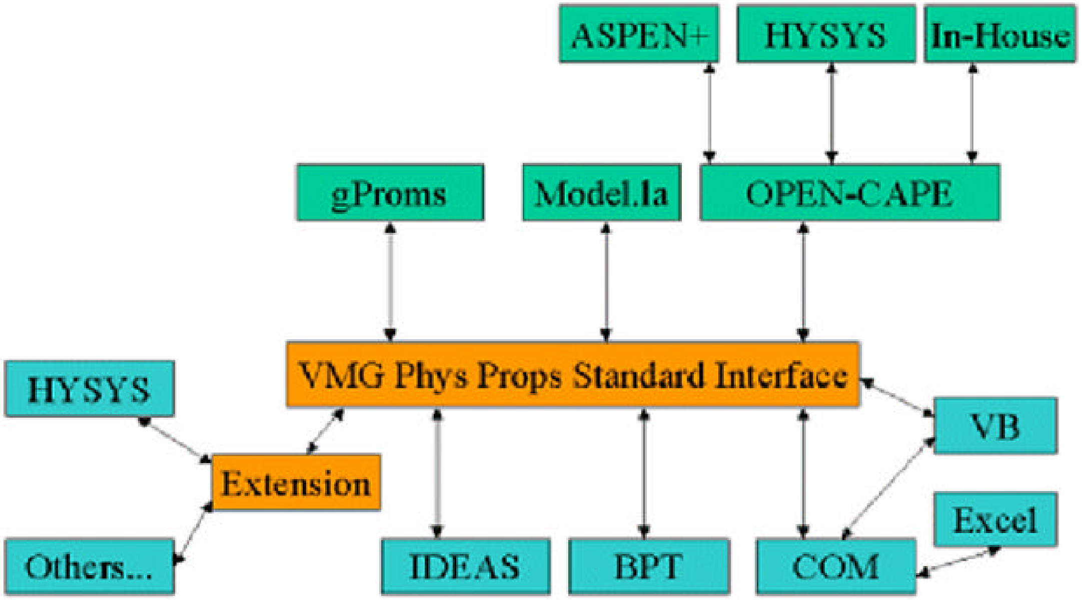
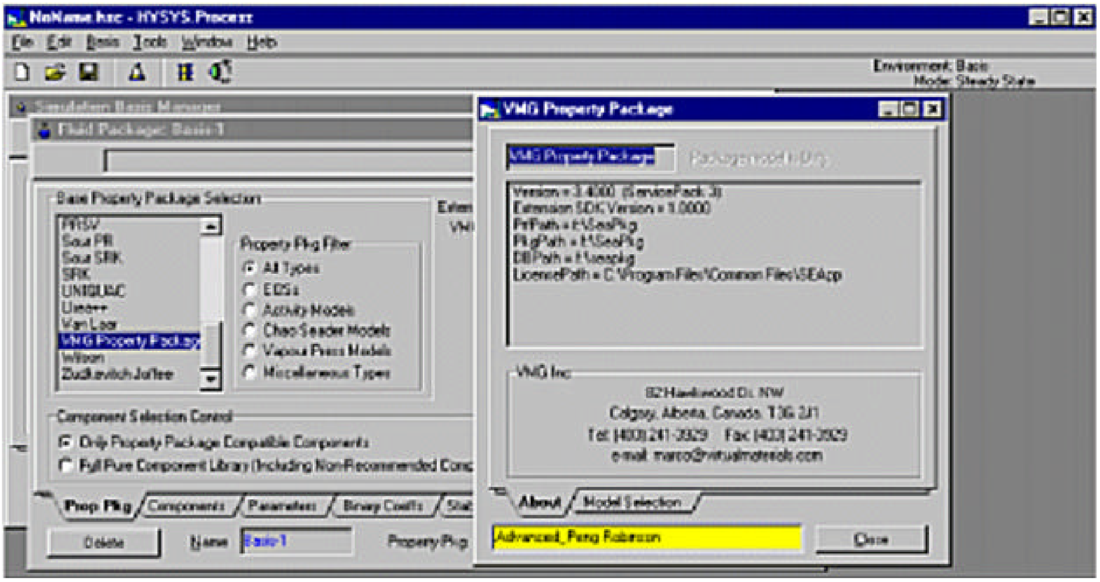


Figure 11: Property Package System Interfaces

This modern approach to software engineering provides immediate benefit to the user. Usually a process engineer will be familiar with a process simulator. By installing our property package system in his or her computer, the user has immediate access to the physical property calculations provided by our physical property system without having to learn how to use a new process simulator. For example, the HYSYS process simulator was built with an open software architecture in mind, and our property package provides an interface, which HYSYS can recognize. From that point on, the user can select our property package system directly from inside the simulator:



Environment: Basis
Mode: Steady State

Name: Basis-1

VMG Property Package

Version = 3.4000 (ServicePack 3)
Extension SDK Version = 1.0000
PrPath = E:\SeaPkg
PkgPath = E:\SeaPkg
DBPath = E:\seapkg
LicensePath = C:\Program Files\Common Files\SEApp

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Advanced_Peng Robinson

Figure 12: Selecting Virtual Materials Group Property Package System from inside the HYSYS Process Simulator

Figure 12 shows what the user of the HYSYS process simulator would see in the basis environment. The basis is the section of the program where thermodynamic models and components are selected for the simulation. Note the Virtual Materials Group Property Package System appears in the Base Property Package Selection scrollable list. With VMG Property Package selected, the form displayed on the right appears, where the user can select the appropriate Virtual Material to represent his or her system of interest as shown in Figure 13.

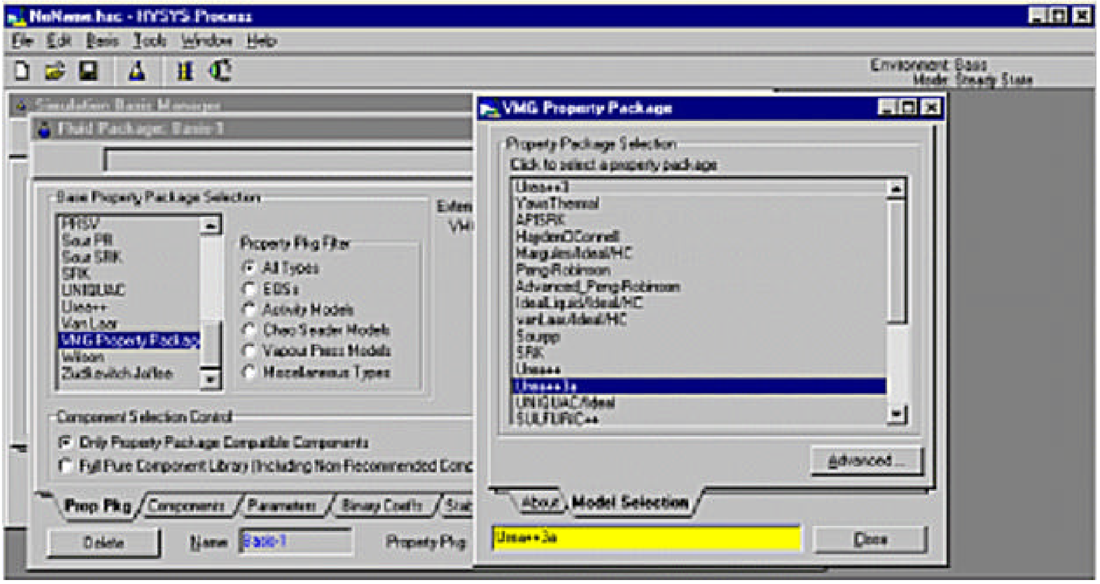


Figure 13: Selecting a Virtual Material to represent a specific process

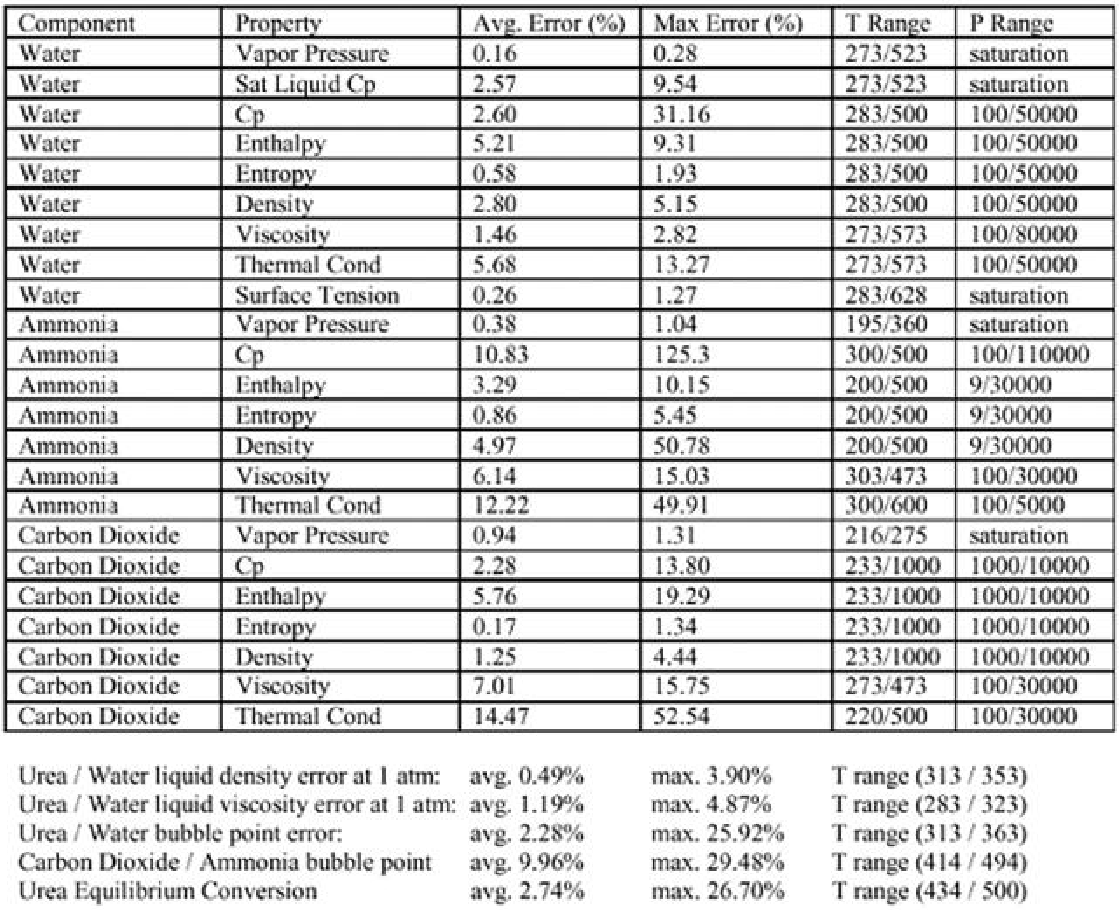
Hardware Like Software

We believe that software to be useful for engineers should behave like a piece of hardware. This has two significant conceptual implications:

1. Software should be able to be plugged into other applications without any intervention from the software vendor. This was explored in the previous item.
2. Users should know how good and how bad the software is when used to simulate his process. Virtual Materials Group performs extensive validations on its property packages and is able to create a "boiler plate" for each property package it produces, thus allowing engineers to know a-priori the performance of a property package. This in turn allows the user to critically evaluate the performance of the property package and interact with Virtual Materials in the event errors are not reported for a specific condition of interest.

Validation of property package systems is a fundamental part of an industrial grade property package system and considerable effort is spent in this feature before a property package is actually released. For example, UREA++ 2.0's boilerplate is reproduced in Table 3.

Table 3: UREA++ Version 2.0 Boiler Plate – Temperatures (K) and Pressures (kPa)



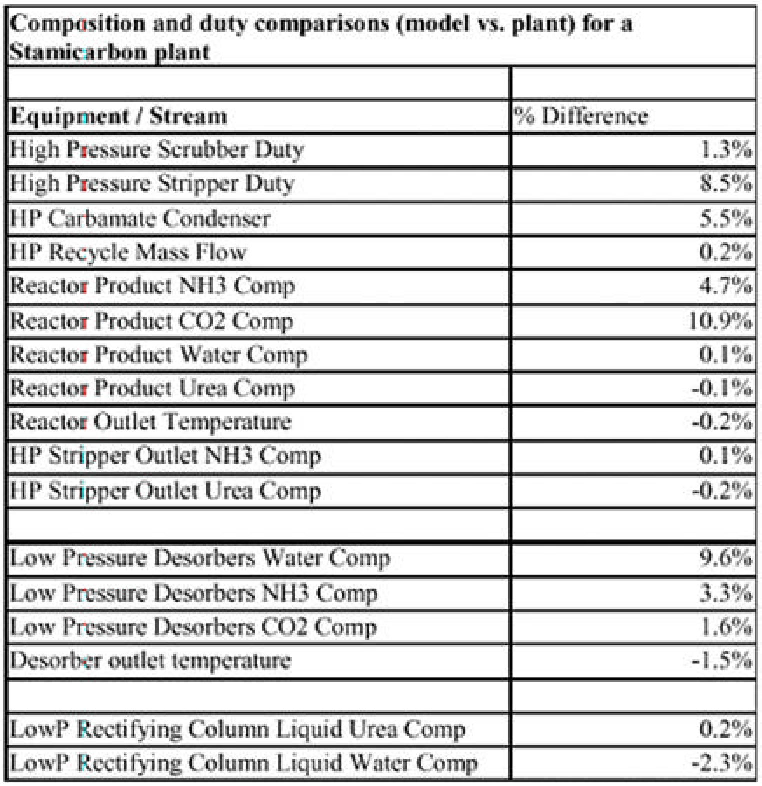
Component	Property	Avg. Error (%)	Max Error (%)	T Range	P Range
Water	Vapor Pressure	0.16	0.28	273/523	saturation
Water	Sat Liquid Cp	2.57	9.54	273/523	saturation
Water	Cp	2.60	31.16	283/500	100/50000
Water	Enthalpy	5.21	9.31	283/500	100/50000
Water	Entropy	0.58	1.93	283/500	100/50000
Water	Density	2.80	5.15	283/500	100/50000
Water	Viscosity	1.46	2.82	273/573	100/80000
Water	Thermal Cond	5.68	13.27	273/573	100/50000
Water	Surface Tension	0.26	1.27	283/628	saturation
Ammonia	Vapor Pressure	0.38	1.04	195/360	saturation
Ammonia	Cp	10.83	125.3	300/500	100/110000
Ammonia	Enthalpy	3.29	10.15	200/500	9/30000
Ammonia	Entropy	0.86	5.45	200/500	9/30000
Ammonia	Density	4.97	50.78	200/500	9/30000
Ammonia	Viscosity	6.14	15.03	303/473	100/30000
Ammonia	Thermal Cond	12.22	49.91	300/600	100/5000
Carbon Dioxide	Vapor Pressure	0.94	1.31	216/275	saturation
Carbon Dioxide	Cp	2.28	13.80	233/1000	1000/10000
Carbon Dioxide	Enthalpy	5.76	19.29	233/1000	1000/10000
Carbon Dioxide	Entropy	0.17	1.34	233/1000	1000/10000
Carbon Dioxide	Density	1.25	4.44	233/1000	1000/10000
Carbon Dioxide	Viscosity	7.01	15.75	273/473	100/30000
Carbon Dioxide	Thermal Cond	14.47	52.54	220/500	100/30000

Urea / Water liquid density error at 1 atm:	avg. 0.49%	max. 3.90%	T range (313 / 353)
Urea / Water liquid viscosity error at 1 atm:	avg. 1.19%	max. 4.87%	T range (283 / 323)
Urea / Water bubble point error:	avg. 2.28%	max. 25.92%	T range (313 / 363)
Carbon Dioxide / Ammonia bubble point	avg. 9.96%	max. 29.48%	T range (414 / 494)
Urea Equilibrium Conversion	avg. 2.74%	max. 26.70%	T range (434 / 500)

Putting It All Together

Several different urea production flowsheets were successfully modeled using the physical behavior modeled by Virtual Materials Property Package System and the calculation sequencing provided by AEA's Software Engineering process simulator HYSYS. Engineers can be productive from the start by having access to rigorous thermodynamic calculations while not having to learn a new process simulation tool. Table 4 summarizes the typical errors found when modeling a urea plant using UREA++.

Table 4: Model versus actual plant comparisons



Composition and duty comparisons (model vs. plant) for a Stamicarbon plant	
Equipment / Stream	% Difference
High Pressure Scrubber Duty	1.3%
High Pressure Stripper Duty	8.5%
HP Carbamate Condenser	5.5%
HP Recycle Mass Flow	0.2%
Reactor Product NH3 Comp	4.7%
Reactor Product CO2 Comp	10.9%
Reactor Product Water Comp	0.1%
Reactor Product Urea Comp	-0.1%
Reactor Outlet Temperature	-0.2%
HP Stripper Outlet NH3 Comp	0.1%
HP Stripper Outlet Urea Comp	-0.2%
Low Pressure Desorbers Water Comp	9.6%
Low Pressure Desorbers NH3 Comp	3.3%
Low Pressure Desorbers CO2 Comp	1.6%
Desorber outlet temperature	-1.5%
LowP Rectifying Column Liquid Urea Comp	0.2%
LowP Rectifying Column Liquid Water Comp	-2.3%

Conclusions and Future Work

A rigorous, general-purpose model for urea production processes was successfully implemented and experimentally verified against actual plant data. The model was implemented using modern software technology, which allows the model to be used in process simulators or other applications such as spreadsheets or operator training software. Currently work is being done in further refining the low and medium pressure thermodynamic models and in the creation of a mass transfer based high-pressure steady state decomposer model.

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