Aspen Plus Urea Synthesis Loop Model

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1 Introduction

This document describes the steady-state Aspen Plus® model of the high-pressure synthesis loop of a urea plant, with a capacity of about 1,100 metric tons of prilled urea per year.
This simulation is based on the Stamicarbon CO_2 Stripping Process, which is a popular and fast growing process for manufacturing urea.
The work demonstrates the capability of Aspen Plus to rigorously model the urea synthesis process. The modeling is complicated due to the formation of ammonium carbamate, an intermediate product for which a special property package has to be developed. This type of model is useful to analyze the plant performance and to improve plant operation, including:

- Energy saving studies to improve economics of the plant.
- Studies of individual pieces of equipment with a view of increasing their throughput and/or improving their performance.
- Flowsheet modification for better plant operation.
- Identifying bottlenecks.
- As a basis for optimization study and for developing on-line control system of the plant.

While this document describes the simulation of the Stamicarbon CO_2 stripping process, the accurate results obtained support the applicability of Aspen Plus and the data package to other urea processes.

Components and Units of Measurement

The table below lists the components modeled in the simulation.

Components

Component Name	Component ID	Type	Formula
Water	H2O	CONV	H_2O
Ammonia	NH3	CONV	H_3N
Carbon Dioxide	CO2	CONV	CO_2
Urea	UREA	CONV	CH_4N_2O
Ammonium Carbamate	CARB	CONV	$CH_6N_2O_2$
Nitrogen	N2	CONV	N_2
Oxygen	O2	CONV	O_2

A small amount of biuret ($C_2H_5N_3O_2$) is produced during the synthesis. In this work, the biuret production is not considered, but the component can easily be added if required.

The pure component properties of all the components except ammonium carbamate can be retrieved from the Aspen Plus databanks. Special efforts were made to incorporate pure component properties of ammonium carbamate in the simulation.

A special contribution of this work is the development of a physical property model to describe the simultaneous physical-chemical equilibrium occurring in the urea-synthesis process.

Metric units are used in this work, except that temperature unit is °C, pressure unit is kg/cm^2 (abs), enthalpy flow unit is mmcal/hr, and mole flow unit is kmol/day.

3 Process Description

A simulation flowsheet of the synthesis loop is shown in Figure 1.

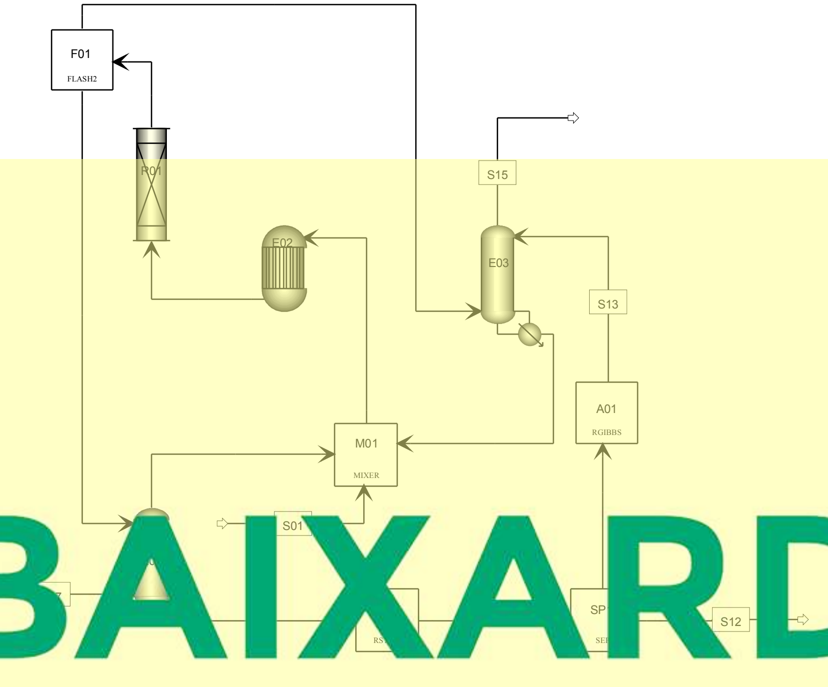

Figure 1: Simulation Flowsheet of Urea Synthesis Loop

The high-pressure loop is operated at around 141 kg/cm^2 (abs) and consists of the following key pieces of equipment:

Equipment	Purpose
R01	Urea Reactor, where ammonium carbamate is dehydrated to urea
E01	H.P. CO2 Stripper, where the bulk of the unreacted carbamate from the reactor effluent is decomposed by stripping with CO2 gas and with heat input.
E02	H.P. Condenser, where the gaseous CO2 and NH3 condense and react to form ammonium carbamate.
E03	H.P Scrubber, where the recycled carbamate solution from the downstream low-pressure section is used to absorb unreacted gases from the reactor.

The process is described as follows:

- Feed CO_2 gas (S07) is fed to the CO_2 stripper, E01, to strip the urea solution coming from the reactor. In the stripper, ammonium carbamate decomposes, liberating more NH_3 and CO_2 to be stripped out. Heat is supplied on the shell side of tubes by condensing 285 psig steam while the urea solution falls inside the tubes countercurrently down past the rising CO_2 stripping gas. The outlet liquid solution from the stripper is rich in urea and goes to the downstream section for urea purification.
- In the adiabatic urea reactor, R01, an aqueous solution of NH_3 and CO_2 (much in the form of ammonium carbamate) and vapors flow upward through 8 stages of reactor volume to minimize back-mixing and provide enough residence time for urea formation. Remaining gases condense and carbamate decomposes in the reactor to provide heat for the slightly endothermic reaction of carbamate to urea. The urea solution (S06) overflows from the top of the reactor back to the Stripper E01, while the unreacted gases (S05) pass out the top of the reactor.
- These unreacted gases pass to the Scrubber, E03, where recycled carbamate solution from the Evaporation/Recirculation section (S13) is passed over the top of a packed bed and fills the tube side section of vertical tubes. The gases rise up through the tubes and pass up through the packed section before leaving the top of the vessel. The contact with the carbamate solution absorbs the unreacted NH_3 and CO_2, while the inert gases of O_2, N_2, and others (S15) vent out from the top. On the bottom, recirculated cooling water flowing inside tubes removes the heat of absorption from the carbamate solution. Carbamate solution (S17) overflows out of the vessel.
- The solution (S17) together with the top vapor stream from the Stripper (S08) is fed to the Carbamate Condenser, E02, through the use of an ejector, where the ammonia feed (S01) serves as the pumping fluid. Ammonium carbamate forms in this condenser. The vapor-liquid mixture (S03) falls through tubes and the heat of reaction is removed by generation of 50 psig steam on the shell [illegible] The mixture goes to [illegible] bottom of the reactor for urea production.
- [illegible] bottom stream (S09) from the Stripper E01 is sent [illegible] the downstream section to recover urea. The recycle stream after recovering the urea (S13) is back to the H.P. Scrubber to complete the loop.

4 Physical Properties

The model for the thermodynamic properties of the NH_3-CO_2-H_2O-UREA-CARB-N_2-O_2 system is based upon the SR-POLAR model within Aspen Plus (Soave, 1972; Peneloux and Rauzy, 1982; Schwartzentruber and Renon, 1989). The model uses an equation of state and is thus suitable for the high-pressure, high-temperature conditions of urea synthesis. Further, the model contains extensions that enable an accurate description of the phase and chemical equilibria, the density and the other thermodynamic properties (e.g., enthalpy) of this system.

We chose our approach to the modeling of the thermodynamic properties after studying the previous modeling attempts in the literature and analyzing the available data. Fréjacques (1948), Kawasumi (1952, 1953 and 1954) and Lemkowitz (1980) developed chemical and thermodynamic models by postulating reactions for urea formation and various simplified assumptions for the phase non-ideality. The simplifying assumptions do not permit an accurate and general model for the chemical-thermodynamic properties. Bernadis et al. (1989) and Isla et al. (1993) developed improved theoretical models by including ionic species and describing the nonideality of the liquid phase by a modified UNIQUAC model. We believe that under the high temperatures (160 to 200°C) and the relatively low water concentrations of urea synthesis, the extent of ionization will be small. Further, modern equations of state such as the SR-POLAR model are well suited to the description of the thermodynamic properties of nonideal systems at high pressures and temperatures. Thus we have chosen to use the SR-POLAR model as the physical-property option.

Development of a data package for this system is difficult since most of the data are only available as combined physical and chemical equilibria. Disassociation pressure data are available for ammonium carbamate (Janacke, 1930), which is the pressure at a specified temperature where ammonia and carbon dioxide are in equilibrium with the condensed-phase ammonium carbamate. Data are also available for the equilibrium conversion of defined mixtures of NH_3-CO_2-H_2O to urea (Kawasumi, 1952, 1953 and 1954; Inoue, 1972). Finally, bubble pressures have been measured for defined mixtures of NH_3-CO_2-H_2O at chemical equilibrium. The Aspen Plus data analysis capabilities (DRS and DATA-FIT) have been used to obtain a simultaneous good fit of these varied and complex sets of data.

Gorlovskii and Kucheryavyi (1979) have analyzed the urea conversion data reported by many authors and have produced an empirical correlation that is recognized to be accurate. Figure 2 compares the equilibrium conversions predicted by the present AspenTech model with the Gorlovskii-Kucheryavyi correlation. The present correlation clearly provides an accurate fit of the data.

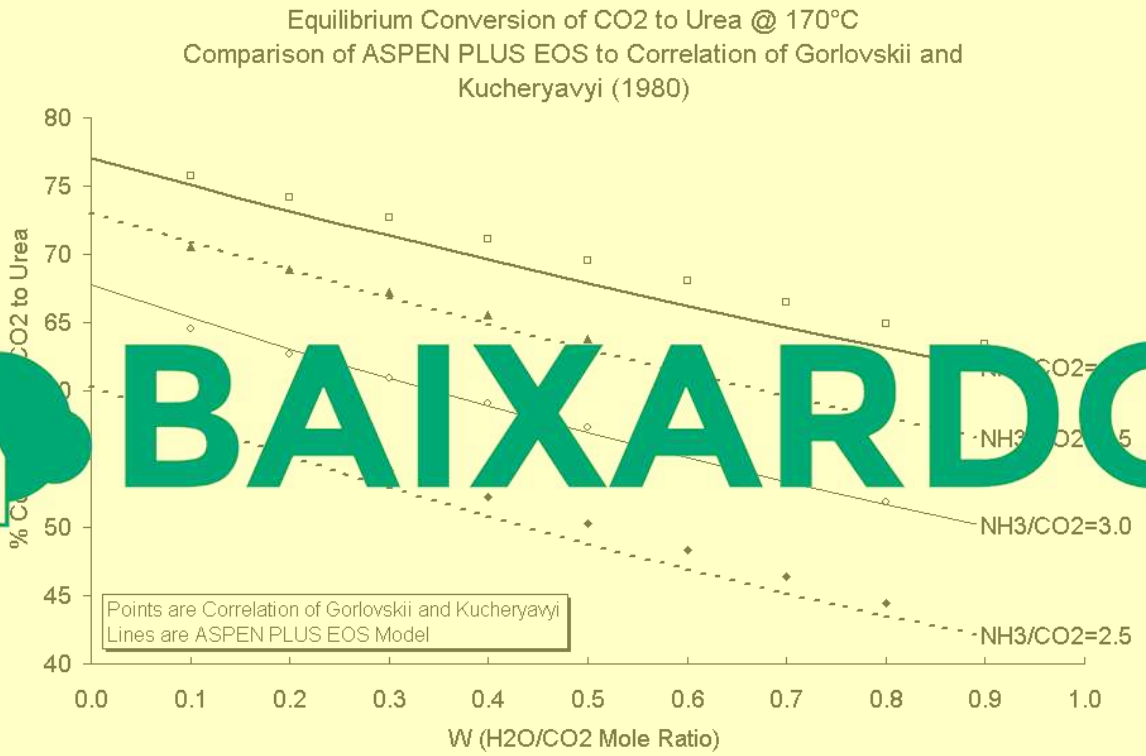

Figure 2: Equilibrium Conversion of CO2 to Urea at 170°C Comparison of Aspen Plus® EOS to Correlation of Gorlovskii and Kucheryavyi (1980)

Figure 3 presents a comparison between the present AspenTech model and the bubble pressure data measured by Lemkowitz (1971, 1972 and 1977). The model provides an accurate description of the data and, in particular, provides an accurate description of the minimum in bubble pressure, which is necessary for an effective description of the urea synthesis process.

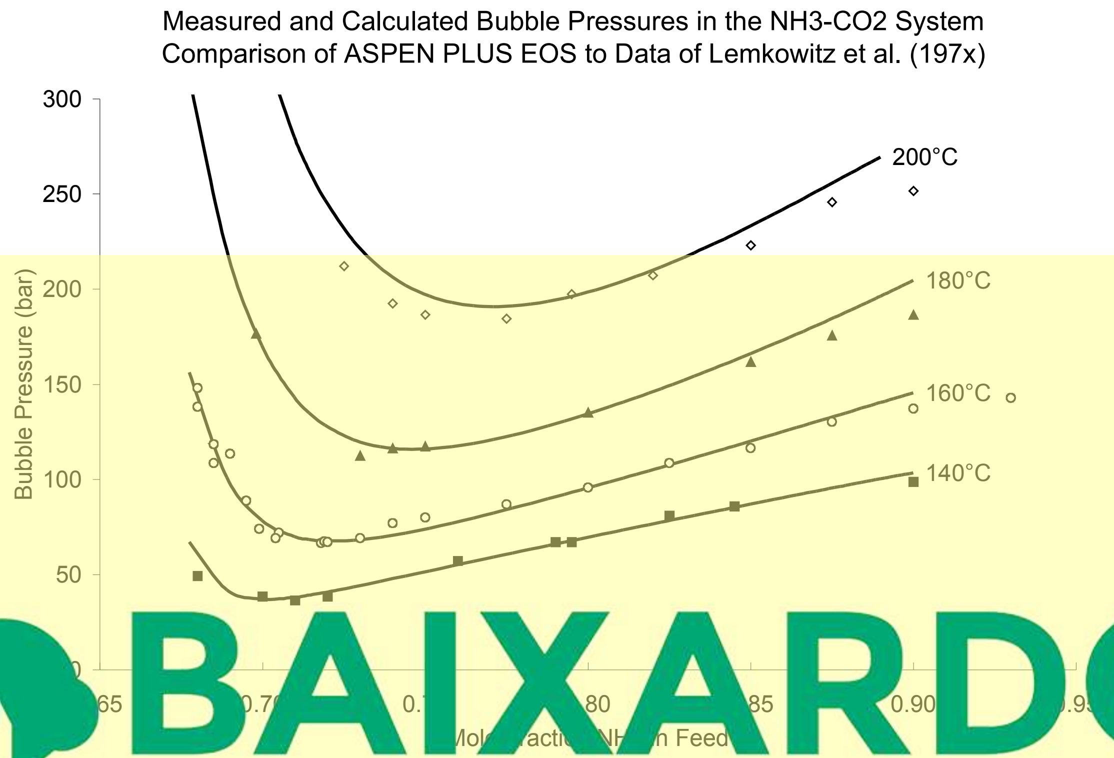

Figure 3: Measured and Calculated Bubble Pressures in the NH3–CO2 System Comparison of Aspen Plus® EOS to Data of Lemkowitz et al. (197x)

The AspenTech model provides an accurate description of the phase and chemical equilibria related to urea synthesis. It also accurately describes the other properties needed for reliable simulations, namely enthalpies and densities.

5 Chemical Reactions Kinetics

There are two main reactions that take place in the urea synthesis process:

(1) $2NH_3 + CO_2$ ¬——→ CARB

(2) CARB ¬——→ UREA + H2O

The first reaction, which takes place in the liquid phase, converts ammonia and carbon dioxide into ammonium carbamate. This reaction is highly exothermic and fast. Chemical equilibrium is readily reached under the operating conditions in the reactor. The second reaction also takes place in the liquid phase and is endothermic. Its rate is slow and equilibrium is usually not reached in the reactor.

A user subroutine, USURA.F, was developed to include the reaction kinetics of both reactions. USURA.F is used in the reactor simulations. Both forward and reverse reactions were considered. The kinetics of Reaction 1 has been set to be rapid so that equilibrium is effectively reached. Limited literature data were used for the kinetics of Reaction 2.

The reaction kinetics has been formulated to approach the equilibrium composition for large residence times. The equilibrium has been described in terms of the fugacity coefficients since an equation of state is used as the thermodynamic model. The equilibrium constant for Reaction 1, in terms of mole fractions, is written as follows:

$$K_1 = \exp\left\{\frac{-\left(G^0_{CARB} - 2G^0_{NH3} - G^0_{CO2}\right)}{RT}\right\}\left(\frac{P}{P^0}\right)^2\left[\frac{\phi^2_{NH3}\phi_{CO2}}{\phi_{CARB}}\right]$$

Where,

T - Temperature
P - Pressure
x - Mole fraction vector
R - Gas constant
P^0 - Reference pressure (= 1 atmosphere)
G_i^0 - Ideal-gas Gibbs Free energy of component i at T, P^0
ϕ_i - Fugacity coefficient of component i at T, P, $\underline{x}$

The equilibrium constant for Reaction 1 in terms of mole fractions is as follows:

$$K_1 = \frac{x_{CARB}}{x^2_{NH3}x_{CO2}}$$

Similar equilibrium equations can be written for Reaction 2.

The rates for Reactions 1 and 2, in units of kmol/s/m^3, are as follows:

$$Rate_1 = k_1\left\{x^2_{NH3}x_{CO2} - \frac{x_{CARB}}{K_1}\right\}$$

$$Rate_2 = k_2\left\{x_{CARB} - \frac{x_{UREA}x_{H2O}}{K_2}\right\}$$

The two rate expressions have been formulated so that they will necessarily reach equilibrium at large residence times. The rate constant for Reaction 1 (K_1) is set to a large value so that this reaction is essentially at equilibrium. The rate constant for Reaction 2 determines the urea conversion in the reactor. Only scant information is available to determine K_2 and it is usually best to adjust its value to fit plant data. A reasonable approximation for K_2 is the following:

$$k_2 = 15.*10^8 e^{\left(-\frac{100.*10^6}{RT}\right)} / v^L$$

Where R=8314.3 and V^L is the molar volume of the liquid.

6 Simulation Approach

The CO_2 Stripper, E01, is of the falling film type, which was approximated by a RADFRAC (multistage distillation) block with 10 stages. Heat is supplied to the stages 2-9 to simulate the heat transfer from the tubes. The urea solution, falling down on tube walls, is stripped off volatile NH3 by the entering CO_2 gas (S07). On each stage the model considers the equilibrium of carbamate in the liquid as well as the VLE of the mixture. Note that the kinetics of carbamate formation is large enough to ensure that chemical equilibrium for the carbamate reaction is reached in each stage of the RADFRAC block.

The Urea Reactor R01, 7.52 ft in diameter and 95 ft in length, is modeled with an RPLUG block. The kinetics is provided by the user subroutine USURA in the RPLUG block.

In the reactor, the exothermic carbamate reaction and the endothermic urea formation reaction are taking place. The reactor is designed such that its volume is big enough for the desired urea production.

The H.P. Scrubber is modeled using a 5-stage RADFRAC block. Heat is taken out from the bottom stage. Similar to the Stripper, E01, on each stage the model considers the equilibrium of carbamate in the liquid as well as the VLE of the mixture.

The E02 H.P. CO_2 Condenser is modeled with an RSTOIC block. A Design Specification paragraph is included to monitor the specified reactor outlet temperature of 183°C by adjusting the extent of the carbamate reaction in E02.

This simulation is based on a closed-loop flowsheet. The downstream section is approximated by using [illegible] block to [illegible] the Stripper bottom urea solution (S09) to [illegible] recycled carbamate solution (S1[illegible]).

7 Simulation Results

The Aspen Plus run was made using Version 206.5. Some of the results are shown below, and a simulation flowsheet with stream data is shown in Figure 4. The simulation results of this generic model are reasonable compared with similar plant operations.

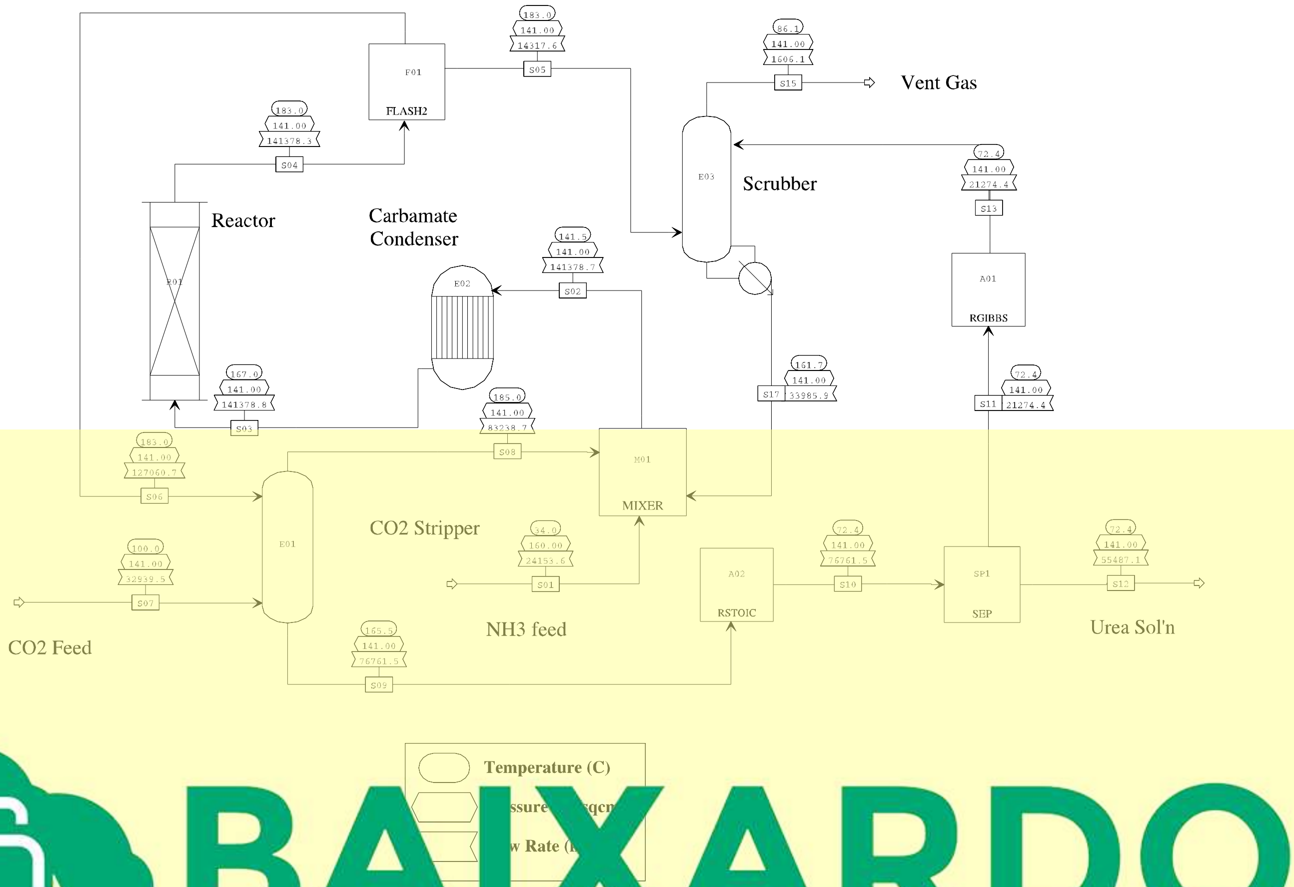

Figure [illegible]: Simulation Flowsheet of Urea Synthesis Loop

Key Process Simulation results:

Equipment	Variable	Value	Unit
R01 – Reactor	Heat duty	0	mmkcal/hr
	Top temperature	183.0 (spec.)	ºC
	Urea in exit stream	42,752	kg/hr
E01 – CO_2 Stripper	Heat duty	16.0 (spec.)	mmkcal/hr
	Top temperature	185.0	ºC
	Bottom temperature	165.6	ºC
	Top stream (S08),	83,239	kg/hr
	Bottom stream (S09),	76,761	kg/hr
	Urea production	42,636	kg/hr
E02 - CO_2 Condenser	Heat duty	-17.92	mmkcal/hr
	Exit temperature	167 (spec.)	ºC
E03 - Scrubber	Heat duty	-3.2 (spec.)	mmkcal/hr
	Top temperature	86.1	ºC
	Bottom temperature	161.7	ºC
	Top stream (S15)	1606.1	kg/hr
	Bottom stream (S17)	33,986	kg/hr

8 Conclusions

1. This urea process model has been developed using Aspen Plus Version 2006.5. This is a rigorous closed-loop model for the plant while the recovery section is approximated by using a SEP model. The carbon dioxide compression section is not included. From the results, it is shown that the SR-POLAR property package used for simulation is appropriate.
2. For further refinement of the model, the following upgrades should be made:
   a) The cooling water circuit for E03 and the low pressure steam circuit for E02 should be implemented. This implementation is useful for energy saving studies.
   b) E02 is simulated in this work by a RSTOIC model. However, a RPLUG model is more suitable for the simulation of this equipment. However, to do so, detailed equipment data for E02 are needed.
   c) The stripper E01 is a falling-film type equipment. It embodies VLE equilibrium, mass transfer, reaction, and heat transfer. To rigorously simulate this equipment, rate-based calculations (RateSep) should be used. A special subroutine will be needed to incorporate the mass transfer limitations of the falling-film. In this simulation, the RADFRAC model was used with component efficiencies for NH_3, CO_2 and H_2O as a work around.
3. The accurate results obtained in the present simulation indicate that Aspen Plus and the physical-property data package will provide accurate simulations of other urea processes.