Aspen Plus

Aspen Plus Ammonia Model

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Contents

1 Introduction

This model simulates an Ammonia Production process using natural gas as a feedstock. This model includes the following features:

- A set of chemical species and property parameters for this process.
- Typical process areas including: Desulfurization, Reforming Unit, Carbon Monoxide Conversion, Carbon Dioxide Removal, Methanation Unit, Synthesis Unit, Refrigeration and the main streams connecting these units.
- Usability features such as an Excel file which allows the user to collect simulation results from the synthesis reactor.
- Definition of property model parameters with user data.

2 Components

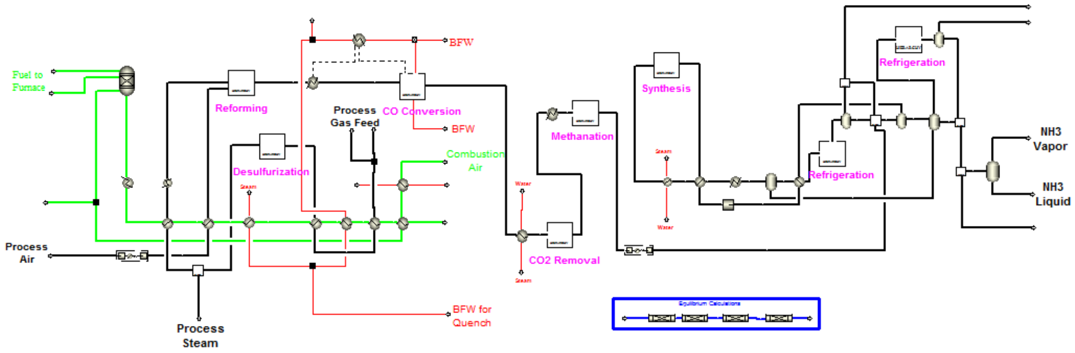
The table below lists the components modeled in the ammonia plant model.

Component ID	Type	Component name	Formula
NH3	CONV	AMMONIA	NH_3
H2	CONV	HYDROGEN	H_2
N2	CONV	NITROGEN	N_2
CH4	CONV	METHANE	CH_4
AR	CONV	ARGON	Ar
CO	CONV	CARBON-MONOXIDE	CO
CO2	CONV	CARBON-DIOXIDE	CO_2
H2O	CONV	WATER	H_2O
O2	CONV	OXYGEN	O_2
C2H6	CONV	ETHANE	C_2H_6
C3H8	CONV	PROPANE	C_3H_8
N-BUTANE	CONV	N-BUTANE	C_4H_{10}
I-BUTANE	CONV	ISOBUTANE	C_4H_{10}
N-PENTAN	CONV	N-PENTANE	C_5H_{12}
I-PENTAN	CONV	I-PENTANE	C_5H_{12}
N-HEXANE	CONV	N-HEXANE	C_6H_{14}
N-HEPTAN	CONV	N-HEPTANE	C_7H_{16}
SULFUR	CONV	SULFUR-8-ATOMIC-GAS	S8
H2S	CONV	HYDROGEN-SULFIDE	H2S
H3O+	CONV	H3O+	H3O+
OH-	CONV	OH-	OH-
NH4+	CONV	NH4+	NH4+
NH2COO-	CONV	CARBAMATE	NH2COO-
HCO3-	CONV	HCO3-	HCO3-
CO3--	CONV	CO3--	CO3-2
NH4HCO3S	SOLID	AMMONIUM-HYDROGEN-CARBONATE	NH4HCO3
NH4HCO3	CONV	AMMONIUM-HYDROGEN-CARBONATE	NH4HCO3

Every component is not included in all the plant sections in order to keep the model as simple as possible. The higher hydrocarbons (C2-C7) are only included in the reformer section. The CO2 Removal section only includes ions and electrolytes. The synthesis and refrigeration sections only include the components H2, N2, Ar, CH4, NH3 and H2O.

3 Process Description

Ammonia is produced basically from water, air, and energy. The energy source is usually hydrocarbons, thus providing hydrogen as well, but may also be coal or electricity. Steam reforming of light hydrocarbons is the most efficient route, with about 77% of world ammonia capacity being based on natural gas.



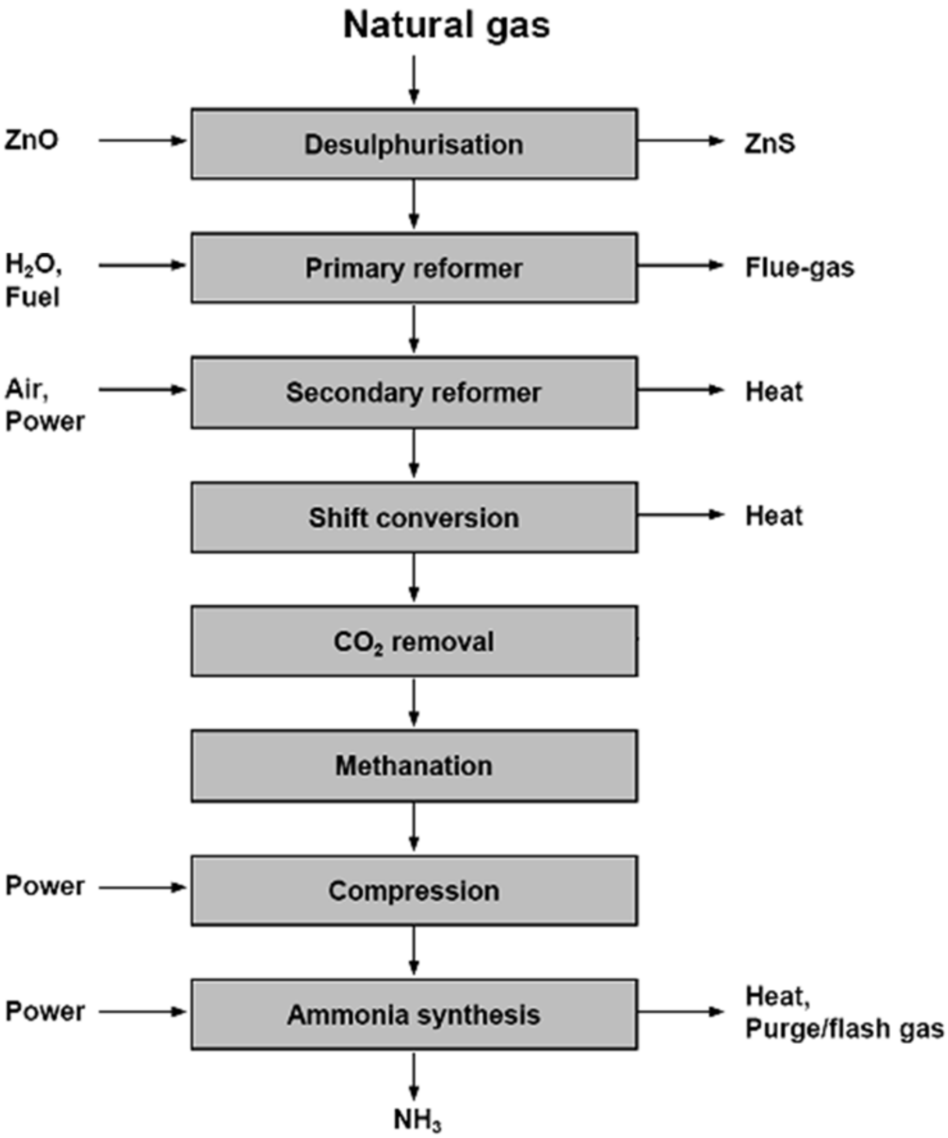


Figure 1 – Block diagram of the steam/air reforming process.

Ammonia plants using natural gas as a feedstock include the following units:

Natural Gas Desulfurization

The natural gas is delivered as dry gas containing a maximum of 40 ppm by weight of sulfur, which is a poison for the reformer catalyst. The desulfurization unit reduces the sulfur content to about 5 ppm by hydrogenating it to hydrocarbons and hydrogen sulfide and then absorbing the hydrogen sulfide in zinc oxides.

Reforming Unit

This unit contains two sections, one is primary reforming, and another is secondary reforming. The desulfurized hydrocarbon feed is reformed to hydrogen and carbon oxides in the presence of steam in the primary reformer, and additionally with hot air in the secondary reformer. The reformed gas contains about 0.3 vol% CH_4.

Carbon Monoxide Conversion

In the CO-shift conversion, the major part of the CO contained in the reformed gas is catalytically converted to CO_2 in two catalytic stages, the first at high temperature and the second at low temperature.

Carbon Dioxide Removal

The carbon dioxide is removed from the converted gas in the CO_2 removal. CO_2 is captured by NH_3 and it will generate ammonium hydrogen carbonate as byproduct. The purified gas with about 0.1 vol% CO_2 is called synthesis gas.

Methanation Unit

Even small quantities of CO (0.1 vol%) and CO_2 (0.3 vol%) are poisons for the ammonia synthesis catalyst. Thus they are reacted to methane over a nickel catalyst. The residual content of CO + CO_2 is less than 10 ppm.

Synthesis Unit

The synthesis gas is pressurized by a centrifugal compressor to approximately 300 bar and hydrogen and nitrogen are catalytically converted to ammonia.

Tailgas Scrubbing

The ammonia in the purge gas from the ammonia unit is recovered in the tailgas scrubbing unit and fed to a refrigeration unit. The treated purge gas is used as fuel for the primary reformer. The building blocks offered in this package do not model this section of the plant.

Refrigeration

The ammonia gas in the synthesis loop is liquefied by ammonia evaporation in the ammonia chiller and discharged as feed to the urea process and to ammonia storage. The building blocks offered in this package do not model this section of the plant.

4 Physical Properties

Equation-of-state models provide an accurate description of the thermodynamic properties of the high-temperature, high-pressure conditions encountered in ammonia plants. The Redlich-Kwong modification RKS-BM was chosen for this application. In most cases, the model parameters were taken from the Aspen physical property databanks. Special accuracy improvements were made to the RKS-BM model as follows:

- The pure-component properties of ammonia were modified to improve the vapor pressure and enthalpy of vaporization, which is important for the synthesis section.
- The binary interaction parameters of H_2, N_2, Ar and CH_4 with ammonia were modified in order to obtain accurate solubilities of these species in ammonia, which is important for the synthesis and refrigeration sections.
- The binary parameters of the air system (N_2, O_2, Ar) were modified in order to enable an accurate simulation of the vapor-liquid equilibrium in the nitrogen plant.

Electrolyte NRTL method and RK equation of state are used to compute liquid and vapor properties respectively in the CO_2 Removal Unit. The NRTL parameters for electrolyte pairs were regressed against VLE data from Maurer (1988) [1]. NH_3 is selected as Henry-components to which Henry's law is applied and the Henry's constants are specified.

5 Chemical Reactions

Reforming Unit

The main reaction occurring in the reformer is the conversion of methane to a mixture of CO, CO_2 and H_2:

$$\mathrm{CH_4 + H_2O \rightarrow CO + 3H_2} \qquad \text{(Endothermic)} \qquad \text{(A-1)}$$

$$\mathrm{CO + H_2O \rightarrow CO_2 + H_2} \qquad \text{(Exothermic)} \qquad \text{(A-2)}$$

The kinetics expression for Reaction A-1, the reforming reaction, (Moe and Gerhard, 1965)[2] is as follows:

$$R = k_2 \frac{K_2 P_{CH_4} P_{H_2O}^2 - P_{H_2}^4 P_{CO_2}}{379} \frac{\text{lb mole}}{\text{hr ft}^3} \qquad \text{(A-3)}$$

The partial pressures are converted to expressions of molar quantities by assuming ideal gas behavior. The factor 379 is needed to convert the units from SCF to moles.

$$R = \frac{k_2 P^3}{SS^3 379}\left[K_2 \left(\mathrm{CH_4}\right)\left(\mathrm{H_2O}\right)^2 - \frac{\left(\mathrm{H_2}\right)^4 \left(\mathrm{CO_2}\right)}{SS^2} P^2 \right] \qquad \text{(A-4)}$$

SS is the total number of moles of mixture per mole of methane fed.

Moe and Gerhard arbitrarily set the P^3 term to 1.0 in order to correlate their data taken from pressures above atmospheric. Therefore, the final form of the model does not have a P^3 term, but is lumped in with the specific rate constant k_2 as:

$$k_2 = A_c e^{\left(\frac{31720}{T+460} - 7.912\right)} \qquad \text{(A-5)}$$

The factor A_c, catalyst activity, is used in the model to give a reasonable reactor performance for the methane conversion. It may be adjusted such that reactor performance matches plant data. The equilibrium constant, K_2, with units of atm^2, is equal to K_1K_3. Hyman (1967) [3]gives:

$$K_1 = \exp\left(-\frac{49,435}{t+460} + 30.707 \right) \text{atm}^2 \qquad \text{(A-6)}$$

$$K_3 = \exp\left(\tfrac{8{,}240}{t+460} - 4.335\right) \text{ below } 1{,}100°\text{F} \tag{A-7}$$

$$K_3 = \exp\left(\tfrac{7{,}351.24}{t+460} - 3.765\right) \text{ above } 1{,}100°\text{F} \tag{A-8}$$

where, t is the temperature in °F.

Chemical equilibrium is assumed for the water shift reaction for which the following holds:

$$K_3 = \frac{(\mathrm{H_2})(\mathrm{CO_2})}{(\mathrm{H_2O})(\mathrm{CO})} \tag{A-9}$$

The reaction kinetics have been implemented in user kinetics Fortran subroutines of the RPlug model. The Fortran subroutines are REFKIN, DRATE, and KFORMC. Subroutines REFKIN and KFORMC are interface routines necessary to interface the Aspen Plus RPlug model with DRATE, the Fortran kinetics subroutine developed by Mok (1982)[4].

The pressure drop expression adopted is as follows:

$$\frac{dP}{dz} = -P_{fact}\left(0.04183 + 0.003292Z - 0.0000395Z^2\right) \tag{A-10}$$

Where,

Z: tube length (ft)

P: pressure (atm)

P_{fact}: pressure drop factor (a function of catalyst characteristics)

or:

$$\Delta P = -P_{fact}\left(0.04183Z + \tfrac{1}{2}0.003292Z^2 - \tfrac{1}{3}0.0000395Z^3\right) \tag{A-11}$$

The pressure drop expression has been implemented as a user pressure drop Fortran subroutine of RPlug model. The Fortran subroutine is REFPD.

Since the net reaction in the primary reformer is endothermic, the heat-transfer rate is critical to the rate of reaction in the tube. The heat-transfer rate is determined by the tube inside and outside heat-transfer coefficients, the flame temperature, and the gas temperature. The heat transfer from the flame to the outside of the tube occurs primarily by radiation. Here an outside heat transfer coefficient is defined for ease of calculation.

$$Flux = ht_{in}\left(T_W - T\right) = ht_{out}\left(T_f - T_W\right) \tag{A-12}$$

The tube-wall temperature T_w is calculated from the second equality.

$$T_W = \frac{ht_{out}T_f + ht_{in}T}{ht_{out} + ht_{in}} \tag{A-13}$$

The flux is in units of BTU/hr/sq ft of inside tube area. The ht_{in} and ht_{out} are the inside and outside heat-transfer coefficients in units of BTU/hr/°F/ft^2 of inside tube-wall area. Both coefficients vary with gas temperature T. The inside heat-transfer coefficient is an overall physical coefficient determined only by the properties of the fluid. Beek (1962) gave the following correlation for estimating ht_{in}:

$$ht_{in} \frac{D_P}{k_f} = 0.4\left[2.58\left(\mathrm{Re}_p\right)^{1/3}\left(\mathrm{Pr}_p\right)^{1/3} + 0.094\left(\mathrm{Re}_p\right)^{0.8}\left(\mathrm{Pr}_p\right)^{0.4}\right] \qquad \text{(A-14)}$$

Hyman (1967) reported that the factor 0.4 is needed to account for the smaller value of ht_{in} when ring-shaped catalyst is used instead of the pellets used by Beck. The calculation of the thermal conductivity k_f, viscosity, and heat capacity were taken from Mok (1982).

The heat-transfer rate outside the tube is assumed to be governed by a radiant heat-transfer mechanism:

$$Flux = \frac{D_{out}}{D_{in}} c\left(T_{f,r}^4 - T_{w,r}^4\right) = ht_{out}\left(T_f - T_w\right) \qquad \text{(A-15)}$$

where D_{in} and D_{out} are the inside and outside diameters of the tube, c is the product of the Stefan-Boltzman constant and the effective emissivity, $T_{f,r}$ and $T_{w,r}$ are the flame temperature and tube-wall temperature in degrees Rankine.

The heat transfer rate was implemented as user heat transfer Fortran subroutines of RPlug model. The Fortran subroutines are REFHT, KFORMC, HTCOEF, TWALL, BPARM, and RKEQ. Subroutines REFHT and KFORMC are interface routines necessary to interface Aspen Plus RPlug model with other Fortran subroutines developed by Mok (1982). HTCOEF computes the heat transfer coefficient. TWALL computes the tube wall temperature. BPARM and RKEQ are physical property routines used to compute transport properties needed in HTCOEF and TWALL.

The primary reformer is generally represented by 1-3 RPlug reactors in series, representing the number of firing zones of the unit in the plant. This allows the fuel requirements of each fired zone to be calculated separately.

The fuel fed to the reformer contains hydrocarbons higher than methane, whereas Equation (A-1) only represents the reforming of methane. These higher hydrocarbons, however, are rapidly converted to methane and are thus accurately modeled using a simple RSTOIC block prior to the reformer tube with the following reactions:

$$\mathrm{3C_2H_6 + H_2O \rightarrow 5CH_4 + CO} \qquad \text{(A-16)}$$

$$\mathrm{3C_3H_8 + 2H_2O \rightarrow 7CH_4 + 2CO} \qquad \text{(A-17)}$$

$$\mathrm{3n\text{-}C_4H_{10} + 3H_2O \rightarrow 9CH_4 + 3CO} \qquad \text{(A-18)}$$

$$\mathrm{3i\text{-}C_4H_{10} + 3H_2O \rightarrow 9CH_4 + 3CO} \qquad \text{(A-19)}$$

$$\mathrm{3C_5H_{12} + 4H_2O \rightarrow 11CH_4 + 4CO} \qquad \text{(A-20)}$$

$$\mathrm{3C_6H_{14} + 5H_2O \rightarrow 13CH_4 + 5CO} \qquad \text{(A-21)}$$

$$\mathrm{3C_7H_{16} + 6H_2O \rightarrow 15CH_4 + 6CO} \qquad \text{(A-22)}$$

The reformer burners are described by RSTOIC blocks in which the combustion is complete. The burner temperature sets the radiant heat-transfer temperature for the reformer tubes; and the heat generated in the burner is equal to the heat absorbed in the reformer tubes. The combination of the RPlug blocks for the reformer tubes and RSTOIC blocks for the burners provides an accurate simulation of the reformer unit.

Carbon Monoxide Conversion

Low-Temperature Shift Reactor

The low-temperature shift reactor is modeled as a plug flow reactor, RPlug.

The reaction stoichiometry considered is:

$$\mathrm{CO} + \mathrm{H_2O} \rightarrow \mathrm{CO_2} + \mathrm{H_2} \tag{A-23}$$

The kinetics expression (Slack, 1974)[5] is as follows:

$$r_{co} = A_c \frac{T_{ref}}{T} \left[\frac{k_{LT} Y_{CO} Y_{H_2O}^{1/2} \left(1 - \frac{K_F}{K_3}\right)}{\frac{1}{P} + k_A Y_{CO} + k_B Y_{CO_2}} \right] \tag{A-24}$$

$$K_F = \frac{(Y_{CO_2})(Y_{H_2})}{(Y_{CO})(Y_{H_2O})} \tag{A-25}$$

where:

Ac	=	catalyst activity
k_{LT}	=	exp (3620/T - 4.32126) standard LT catalyst activity in lb-mol/hr/ft^3/atm
K_3	=	exp (8240/(t+459.7) - 4.33)
k_A	=	exp (4580/T - 7.4643) atm^{-1}
k_B	=	exp (1500/T - 2.623)atm^{-1}
T_{ref}	=	513.13K
T	=	temperature in K
t	=	temperature in °F

The reaction kinetics has been implemented in a user kinetics Fortran subroutine under the RPlug model. The Fortran rate subroutine is LTKIN, which calls KFORMC for obtaining the component locations.

High-Temperature Shift Reactor

The high-temperature shift reactor is modeled as a plug flow reactor, RPlug.

The reaction stoichiometry considered is:

$$\mathrm{CO} + \mathrm{H_2O} \rightarrow \mathrm{CO_2} + \mathrm{H_2} \tag{A-26}$$

The kinetics expression (Slack, 1974) is as follows:

$$\mathrm{CO} + \mathrm{H_2O} \rightarrow \mathrm{CO_2} + \mathrm{H_2} \tag{A-27}$$

$$r_{CO} = A_c K_{HT} P^{1/2} Y_{CO} \left(1 - \frac{K_f}{K_3}\right) \qquad \text{(A-28)}$$

$$K_3 = \exp\left(\frac{8240}{t + 459.7} - 4.33\right) \; below\, 1100°F \qquad \text{(A-29)}$$

$$K_F = \frac{(Y_{\mathrm{CO_2}})(Y_{\mathrm{H_2}})}{(Y_{\mathrm{CO}})(Y_{\mathrm{H_2O}})} \qquad \text{(A-30)}$$

where:

A_c = catalyst activity

k_{HT} = exp (10.3375 - 5787.62/T)
standard HT catalyst activity in lb-mol/hr/ft^3/atm$^{1/2}$

T = temperature in K

t = temperature in °F

The reaction kinetics was implemented in a user kinetics Fortran subroutine under the RPlug model.

The Fortran rate subroutine is HTKIN, which calls KFORMC for obtaining the component locations.

Carbon Dioxide Removal

The electrolyte solution chemistry has been modeled with a CHEMISTRY model with ID of NH3. Chemical equilibrium is assumed with all the ionic reactions in the CHEMISTRY NH3. In addition, a kinetic REACTION model named NH3 has been created. In NH3, all reactions are assumed to be in chemical equilibrium except the reactions of CO2 with OH- and the reactions of CO2 with NH3.

A. Chemistry ID: NH3

1 Equilibrium $2H_2O \leftrightarrow H_3O^+ + OH^-$ (A-31)

2 Equilibrium $CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^-$ (A-32)

3 Equilibrium $HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{-2}$ (A-33)

4 Equilibrium $NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$ (A-34)

5 Equilibrium $H_2NCOO^- + H_2O \leftrightarrow NH_3 + HCO_3^-$ (A-35)

6 Salt $NH_4HCO_3(S) \leftrightarrow NH_4^+ + HCO_3^-$ (A-36)

7 Dissociation $NH_4HCO_3 \rightarrow NH_4^+ + HCO_3^-$ (A-37)

B. Reaction ID: REA-NH3

1	EQUIL	$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$	(A-38)
2	EQUIL	$2H_2O \leftrightarrow H_3O^+ + OH^-$	(A-39)
3	EQUIL	$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{-2}$	(A-40)
4	KINETIC	$CO_2 + OH^- \rightarrow HCO_3^-$	(A-41)
5	KINETIC	$HCO_3^- \rightarrow CO_2 + OH^-$	(A-42)
6	KINETIC	$NH_3 + CO_2 + H_2O \rightarrow H_2NCOO^- + H_3O^+$	(A-43)
7	KINETIC	$H_2NCOO^- + H_3O^+ \rightarrow NH_3 + H_2O + CO_2$	(A-44)
8	Salt	$NH_4HCO_3(S) \leftrightarrow NH_4^+ + HCO_3^-$	(A-45)

The equilibrium expressions for the reactions are taken from the work of Miles et al.[6]. In addition, the power law expressions are used for the rate-controlled reactions (reactions 4-7 in REA-NH3) and the general power law expression is:

$$r = k\left(T/T_0\right)^n \exp\left[\left(\frac{-E}{R}\right)\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]\prod_{i=1}^{N} C_i^{a_i} \qquad \text{(A-46)}$$

If T_0 is not specified, the reduced power law expression is used:

$$r = kT^n \exp\left(-\frac{E}{RT}\right)\prod_{i=1}^{N} C_i^{a_i} \qquad \text{(A-47)}$$

In this file, the reduced expressions are used. In equation A-47, the concentration basis is **Molarity**, the factor n is zero, k and E are given in Table 2. The kinetic parameters for reactions 4-7 in Table 3 are derived from the work of Pinsent[7].

Table 1. Parameters k and E in Equation A-47

Reaction No.	k	E (cal/mol)
4	4.32e+13	13249
5	2.38e+17	29451
6	1.35e+11	11585
7	4.75e+20	16529

The built-in Keq expression (Equation 3) is used for the salt precipitation reaction of NH_4HCO_3,

$$\ln K_{eq} = A + B/T + C\ln\left(T\right) + DT \qquad \text{(A-48)}$$

The parameters A, B and C were regressed against SLE data from Trypuc et al. [8].

Table 3. Parameters A, B and C in Equation A-48

Reaction	A	B	C
NH_4HCO_3 salt precipitation	-914.00821	38648.2117	136.174996

Methanation Unit

The methanation reactor, which removes trace amounts of CO from H_2-rich synthesis feed mixtures, is modeled as a plug flow reactor by RPlug.

Two reactions occur in the methanation reactor:

$$\mathrm{CO} + 3\mathrm{H}_2 \rightarrow \mathrm{CH}_4 + \mathrm{H2O} \tag{A-49}$$

$$\mathrm{CO}_2 + 4\mathrm{H}_2 \rightarrow \mathrm{CH}_4 + 2\mathrm{H}_2\mathrm{O} \tag{A-50}$$

Yadav and Rinker (1993)[9] developed empirical correlations for the methanation of CO (Equation A-49) as part of a laboratory data program. Their correlation, based upon a proposed Langmuir-Hinshelwood mechanism is as follows:

$$r = \frac{AP_{\mathrm{H_2}}^{0.5} P_{\mathrm{CO}}}{1 + BP_{\mathrm{CO}} + CP_{\mathrm{H_2}}^{0.5}} \tag{A-51}$$

where r is the reaction rate in mol/g.s, P refers to partial pressures in kPa, and A, B and C are empirical constants determined at each temperature. Yadav and Rinker (1993) covered a broad range of CO concentrations, but for methanation we are mainly interested in very low CO levels. At low CO concentrations, Equation A-38 simplifies to the following form:

$$r = \frac{A}{C^2} \frac{P_{\mathrm{CO}}}{P_{\mathrm{H_2}}^{0.5}} \tag{A-52}$$

The data reported by Yadav and Rinker at 503, 513 and 529 K were fitted to a simple Arrhenius equation as follows:

$$r = 0.314 e^{\left(1{,}300\left[\frac{1}{T} - \frac{1}{513}\right]\right)} \left\{ \frac{P_{\mathrm{CO}}}{P_{\mathrm{H_2}}^{0.5}} \right\} \tag{A-53}$$

Proper modeling of the methanation must include the effect of the backward reaction as equilibrium is approached. Hence, the complete version of Equation A-53 is as follows:

$$r = A_c 0.314 e^{\left(1{,}300\left[\frac{1}{T} - \frac{1}{513}\right]\right)} \left\{ \frac{P}{P_{\mathrm{H_2}}^{0.5}} \right\} \left[y_{\mathrm{CO}} - \frac{y_{\mathrm{CH_4}} y_{\mathrm{H_2O}}}{y_{\mathrm{H_2}}^3 P^2 K_{\mathrm{CO}}} \right] \tag{A-54}$$

where, P is the pressure in kPa, y is the component mole fraction, K_{CO} is the equilibrium constant for Reaction A-49 and A_c is the catalyst activity factor.

$$K_{\mathrm{CO}} = e^{\left(-38.4523 + 26{,}270/T\right)} \qquad \text{(A-55)}$$

Kinetic data are not available for the methanation of CO_2. We use the same kinetic expression for CO_2 as for CO, recognizing the weakness of this approach, but also recognizing that the concentration of CO_2 in the process stream is very small. The rate of Reaction A-50 is given as:

$$r = A_c 0.314 e^{\left(1{,}300\left[\frac{1}{T} - \frac{1}{513}\right]\right)} \left\{\frac{P}{P_{\mathrm{H_2}}^{0.5}}\right\} \left[y_{\mathrm{CO_2}} - \frac{y_{\mathrm{CH_4}} y_{\mathrm{H_2O}}^2}{y_{\mathrm{H_2}}^4 P^2 K_{\mathrm{CO_2}}} \right] \qquad \text{(A-56)}$$

$$K_{\mathrm{CO_2}} = e^{\left(-33.923 + 21{,}621/T\right)} \qquad \text{(A-57)}$$

Synthesis Unit

The ammonia synthesis converter beds are modeled as a plug flow reactor by RPlug.

The reaction stoichiometry considered is:

$$\mathrm{N_2 + 3H_2 \rightarrow 2NH_3} \qquad \text{(A-58)}$$

The kinetics expression (Nielsen, 1968)[10] is as follows:

$$R = A_c \left[\frac{AK\left(a_N k_{eq}^2 - \frac{a_A^2}{a_H^3}\right)}{\left(1 + K_a \frac{a_A}{a_H^W}\right)^2 \alpha} \right] \frac{\mathrm{kgmole}}{\mathrm{m^3hr}} \qquad \text{(A-59)}$$

where:

A_c = catalyst activity

α = .654

w = 1.523

and where k_{eq} is the equilibrium constant, AK, the specific rate constant, and K_a, the adsorption equilibrium constant.

$$\log_{10} k_{eq} = -2.691122 \log_{10}(T) - 5.519265\times10^{-5} T + 1.848863\times10^{-7} T^2 + \frac{2001.6}{T} + 2.6899 \qquad \text{(A-60)}$$

$$AK = 3.945\times10^{10} \exp\left(-\frac{5622}{T}\right) \qquad \text{(A-61)}$$

$$K_a = 2.94\times10^{-4} \exp\left(\frac{12104}{T}\right) \qquad \text{(A-62)}$$

a_N, a_H, a_A, in Equation (are the activities of nitrogen, hydrogen and ammonia. α and w are parameters. Nielsen also gave the following formula for evaluating the activities:

$$a_i = x_i P \exp\left[\frac{P}{RT}\left(B_i - \frac{A_i}{RT} - \frac{C_i}{T^3} + \left(A_i^{0.5} - \sum x_i A_i^{0.5} \right)^2 \right) \right] \qquad \text{(A-63)}$$

where:

R = Gas constant (=0.0826)

P = Pressure in atm

T = Temperature in K

x_i = mole fraction of component i

The values of A's, B's and C's are listed below:

i	**A_i**	**B_i**	**C_i**
H_2	0.1975	.02096	5.04×10^2
N_2	1.3445	.05046	4.20×10^4
NH_3	2.393	.03415	4.77×10^6
Ar	1.2907		
CH_4	2.2769		

The reaction kinetics has been implemented by a user kinetics Fortran subroutine of RPlug model named SYNKIN. Subroutine SYNKIN calls RNH3, the Fortran kinetics subroutine developed by Mok (1981). Subroutine KFORMC is used to find the component integer variables from the Aspen Plus system.

6 Simulation Approaches

Aspen Plus Unit Operation Blocks Used in Ammonia production Model

Unit Operation	Aspen Plus "Block"	Comments / Specifications
Natural Gas Desulfurization	Sep2 + RStoic	The sulfur is hydrogenated to hydrogen sulfide and then removed
Reforming	RStoic + RPlug	The reactions are defined in the subroutines using RPlug. The reformed gas contains about 0.3 vol% CH_4.
Carbon Monoxide Conversion	RPlug + FSplit + Heater	CO converts to CO_2 in two catalytic stages, the first at high temperature and the second at low temperature.
Carbon Dioxide Removal	Flash2	CO_2 is captured by NH_3.
Methanation	RPlug + Sep2	The residual content of CO + CO_2 is less than 10 ppm.
Synthesis	RPlug + FSplit + Heater	Reacting with RPlug and high pressure.
Refrigeration	Valve + HeatX	Ammonia gas in the synthesis loop is liquefied

Design Spec Used in Ammonia production Model

Spec Name	Spec (Target)	Manipulated Variables
F18	Mass flow of stream S-18 is 44100 kg/hr, the tolerance is 0.1.	The heat duty of Heater E003.

Calculator Used in Ammonia production Model

Name	Purpose
RESULTS	Collect simulation results from the synthesis reactor.

Kinetics Model Implementation

A summary of the Fortran subroutines developed for the kinetics reactors is presented in Table A-1. Table A-2 shows the input parameters to the main subroutines.

Table A-1. Summary of Kinetics Fortran Subroutines

	Primary Reformer	**High Temperature Shift**	**Low Temperature Shift**	**Methanator**	**Synthesis Converter**
Kinetics	REFKIN KFORMC DRATE	HTKIN KFORMC	LTKIN KFORMC	MTHKIN	SYNKIN KFORMC RNH3
Pressure Drop	REFPD				
Heat Transfer	REFHT KFORMC HTCOEF TWALL BPARM RKEQ				

Table A-2. Parameter Input to Kinetics Fortran Subroutines

Main User Subroutine Name	**Parameter**	**Default Value**
REFKIN	R_1 – Catalyst activity	1.0
REFPD	R_1 – Pressure drop factor	1.0
REFHT	R_1 – Flame temperature R_2 – Maximum tube temperature R_3 – Radiative Heat transfer coefficient	975°C 1200°C $1.9*10^{-8}$ kcal/hr/m^2
HTKIN	R_1 - Catalyst activity	1.0
LTKIN	R_1 - Catalyst activity	1.0
MTHKIN	R_1 - Catalyst activity	1.0
SYNKIN	R_1 - Catalyst activity	1.0

7 Simulation Results

Key Stream Simulation Results

Flowsheet Variable		Value	Unit
Feed	Process Air	53000	scmh
	Natural Gas	32000	scmh
	Process Stream	102041	kg/hr
	Fuel to Furnace 1	10184	scmh
	Fuel to Furnace 2	10854	scmh
	Combustion Air	178220	scmh
	BFW	170180	kg/hr
Product	NH_3 (Liquid phase)	3101	kmol/hr

8 Conclusions

The Ammonia model provides a useful description of the process. The simulation has been developed using many of the capabilities of Aspen Plus including unit operation models, physical property methods, models and data, and flowsheeting capabilities like convergence design specs.

The model provides rigorous mass and energy balance information for ammonia production, and can be used to support the conceptual process design. This model also can be used in developing reaction simulations with RPlug. The model is meant to be used as a guide for modeling ammonia production. Users may use it as a starting point for more sophisticated models.

9 References

[1] Goppert U., Maurer G., “Vapor-Liquid Equilibrium in Aqueous Solutions of Ammonia and Carbon Dioxide at Temperatures Between 333 and 393K and Pressure up to 7 MPa”, *Fluid Phase Equilibrium*, Vol. 41,153 (1988)

[2] Moe, J.H. and Gerhard, E.R., Preprint 36d, 56th National Meeting, AIChE, May, 1965.

[3] Hyman, M.H., Computational Study of a Refinery Hydrogen Plant, H.S. Thesis, Univ. of Calif., Berkeley, 1967.

[4] Mok, L-F, Sensitivity Study of Energy Consumption in Ammonia Plant Operation, H.S. Thesis, Univ. of California, Berkeley, 1982.

[5] Slack, A.V. and G.R. James, ed., *Ammonia*, Marcel Dekker, Inc., New York, 1974.

[6] Miles D.H., Wilson G.M., "Vapor liquid Equilibrium Data for Design of Sour Water Strippers", *Annual Report to the API for 1974*, October 1975.

[7] Pinsent B. R., Pearson L., Roughton F. J., “The Kinetics of Combination of Carbon Dioxide with Ammonia”, *Trans. Faraday Soc.*, Vol. 52, 1594 (1956)

[8] Trypuc M., Kielkowska U., "Solubility in the NH4HCO3 + NH4VO3 + H2O System", *J. Chem. Eng. Data*, Vol. 41, 1005(1996)

[9] Yadav, R. and R.G. Rinker, Steady-State Methanation Kinetics Over a Ni/Al2O3 Catalyst, *Can. J. of Chem. Eng.*, 71, 202 (1993).

[10] Nielsen, A., *An Investigation on Promoted Iron Catalysts for the Synthesis of Ammonia*, 3rd ed., Jul. Gjellerups Forlag, 1968.

[11] Beek, J., “Design of Packed Catalytic Reactors”, *Adv. Chem. Eng.*, 3, 203 (1962).