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Empirical Modeling of Urea Synthesis Chemical Equilibria

Moustafa Aly Soliman

Abstract: In this paper empirical formulas for the chemical equilibrium of reactions involved in urea synthesis are derived. Their accuracy is checked against data obtained from the application of Aspen plus to a urea plant based on Stamicarbon technology. The accurate results obtained support their application in the simulation of the reactions involved in urea synthesis.

Keywords: Chemical equilibrium, Empirical modeling, High pressure, Urea synthesis

I. INTRODUCTION

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 is dehydrated into urea and water:

$$2\text{NH}_3(\ell) + \text{CO}_2(\ell) \rightleftharpoons \text{NH}_2\text{COONH}_4(\ell) \quad \Delta H = 157.60 \text{kJ/mol}$$

(1)

$$2\text{NH}_3(\ell) + \text{CO}_2(\ell) \rightleftharpoons \text{NH}_2\text{COONH}_4(\ell) \quad \Delta H = 157.60 \text{kJ/mol}$$

(2)

Reaction 1 is fast, highly exothermic, and goes essentially to completion under normal industrial processing conditions, while reaction 2 is slow, and endothermic. Ammonia is usually in excess and thus conversion is reported as percentage of carbon dioxide reacting.

Different urea production technologies basically differ on how urea is separated from the reactants and how ammonia and carbon dioxide are recycled. Optimization of these production technologies would aim at increasing carbon dioxide conversion, optimization of heat recovery and utility consumption reduction. To achieve these objectives, a simulation code which accurately describes material and energy balances and design equations, is needed.

There are different thermodynamic models with different degrees of complexity. There are models for high pressure, high temperature conditions with ammonia as the main solvent, and there are models for aqueous solutions at low temperature and pressure. At high temperature and pressure, there are models that include all ionic species NH$_4$+, HCO$_3$−, NH$_2$COO−, (Isla et al. [1]), models that contain only molecular species (Satyro et al.[2]) and models that contain no bicarbonate (Lemkowitz et al.[3], Piotrowski et al [4]). This last model assumes that CO$_2$ exists as free CO$_2$ or as Carbamate. Also the models themselves vary in complexity. That of Isla [1] uses UNIQUAC for Liquid and Nikamura et al.[5] for gas whereas that of Piotrowski [4] uses empirical correlations for liquid activities. Hamidipour et al[6] assumes the gas is ideal and the liquid properties are modeled using Wilson equations.

Other papers related to the thermodynamics of urea synthesis are listed in references [7-22]

Reactor models also vary in complexity. Irazoqui et al [23] assume that all components are in liquid phase and there is countercurrent flow between the coil and the bulk of the reactor. Hamidipour et al.[6] assumes that the flow is cocurrent and that CO$_2$ reacts with ammonia in the gas phase to give ammonium carbamate as liquid phase. They include biuret formation in their model. Dente et al. [24,25] assume mass transfer between gas and liquid. One can even assume that the reactor is an equilibrium one and assume certain efficiency for urea formation. Zhang et al [26] assume equilibrium between the gas and liquid phases and that the reactor takes place between liquid phases. Papers [27-29] deal with the reaction of urea to biuret.

II. METHODOLOGY

We thought that if we use a simple empirical thermodynamic model, it might be more useful than a comprehensive model that we do not know for sure the actual concentrations for components like the carbamate and the bicarbonate.

We thus turned our attention to the empirical model of Piotrowski et al 1998 which does not assume the presence of any ionic species, only the reactants and products.

Equation (8) of Piotrowski et al 1998 predicts low conversion to ammonium carbamate. On the other hand Lemkowitz et al 1973 data predicts high conversion to ammonium carbamata. Data obtained from the scrubber of an industrial plant shows high conversion to carbamate because of the large amount of heat that should be removed due to the exothermic reaction of carbamate formation. Thus equation (8), Piotrowski et al 1998 for the equilibrium constant for equation (1) is modified to

$$\text{Log}(K_a) = \frac{4350}{t} - 7.7$$

(3)

where t is temperature in K

Let

a = the ratio of the initial concentration of ammonia to carbon dioxide

b=the ratio of the initial concentration of water to carbon dioxide

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\[ y = \text{the fraction of carbon dioxide converted to urea and ammonium carbamate at equilibrium} \]

\[ st = \text{fraction of carbon dioxide converted to urea at equilibrium} \]

the mole fractions of carbon dioxide \(x_1\), ammonia \(x_2\), water \(x_3\), ammonium carbamate \(x_4\), and urea \(x_5\) are given by

\[ x_1 = \frac{(1-y)}{N} \]  \hspace{1cm} (4)

\[ x_2 = \frac{(a-2y)}{N} \]  \hspace{1cm} (5)

\[ x_3 = \frac{(b+st)}{N} \]  \hspace{1cm} (6)

\[ x_4 = \frac{(y-st)}{N} \]  \hspace{1cm} (7)

\[ x_5 = \frac{st}{N} \]  \hspace{1cm} (8)

\[ N = 1 + a + b - 2y + st \]  \hspace{1cm} (9)

\[ K_1 = \frac{x_4}{x_1^a x_2^b} \]  \hspace{1cm} (10)

Empirical correlations are available for \((st)\). We choose that of Piotrowski et al 1998

\[ st = -3.4792 + 8.2677 \times 10^{-1} a - 1.8998 \times 10^{-2} a^2 \]

\[ -2.3155 \times 10^{-1} b - 1.144 \times 10^{-1} (t/100) \]  \hspace{1cm} (11)

\[ + 2.9879 \times 10^{-2} ab - 1.3294 \times 10^{-1} a(t/100) \]

\[ + 4.5348 \times 10^{-1} (t/100)^2 - 5.5339 \times 10^{-2} (t/100)^3 \]

These data are obtained for the following range of parameters

- \(t\) from 433 to 483 \(K\)
- \(a\) from 2.0 to 6.
- and \(b\) from 0 to 1.2

Using equation (3) the definition of \(K_i\) and equation (10) of Piotrowski et al 1998, we obtain a non-linear equation in \(y\) which is solved for the range of parameters for which equation (11) is obtained.

For the equilibrium conversion of carbon dioxide to urea, we are able to fit the data to the following expression for the equilibrium constant for the conversion of ammonium carbamate to urea (equation (12))

\[ t \ln \left( \frac{x_3 x_5 K_1}{x_4} \right) = c_1 + c_2 a + c_3 a^2 + c_4 b + c_5 ab \]

\[ + c_6 t + c_7 t^2 + c_8 t^3 + c_9 at^2 + c_{10} at + c_{11} a^2 t + c_{12} bt \]

where the \(c\)'s are constants to be determined.

A least square analysis of equation (12) for different values of \(a, b, t\) using MATLAB leads to

\[ K_2 = \frac{x_3 x_5}{x_4} = \exp\left(2938.555-1577.719 a \right) \]

\[ -14.31545 a^2 - 452.6036 b + 51.51285ab \]

\[ + 3.20745 r - 0.032943 r^2 + 4.740364 \times 10^{-3} t^3 \]

\[ - 1.670736 \times 10^{-2} a t^2 + 11.308775 at \]

\[ + 0.0121076 a^2 t + 0.564388 bt / t / K_i \]  \hspace{1cm} (13)

In the next section we apply equations (3,13) to the reactor section of high pressure synthesis loop of a urea plant simulated as an example in Aspen Plus.

III RESULTS AND DISCUSSION

Aspen Plus gave an example of the steady state simulation of the high-pressure synthesis loop of urea plant producing 1050 metric ton per day and is based on the Stamicarbon CO₂ Stripping Process. The model for the thermodynamic properties of the NH₃-CO₂-H₂O-UREA-CARB-N₂-Oₓ system is based upon the SR-POLAR model. This model contains an equation of state and extension for accurate estimation of phase and chemical equilibria. The high-pressure synthesis loop operates at a pressure of about 141 kg/cm² and consists of urea reactor where ammonium carbamate is dehydrated to urea, CO₂ stripper to decompose carbamate present with urea, condenser to form carbamate from CO₂ and NH₃ and scrubber to absorb unreacted gases from the reactor.

The reactor is equipped with sieve plates in order to realize a number of CSTRs (Continuous Stirred Tank Reactors) by which plug flow regime is approached.

The Urea Reactor is 2.2921 m in diameter and 28.956 m in length, and is modeled with an RPLUG block. The kinetics is provided by the user subroutine USURA in the RPLUG block.

The simulation results of this model are reasonable compared with similar plant operations.

For example, a plant which produces 1750 metric ton per day has streams with flowrates of 1.66 (1750/1050) that of Aspen plus model. The diameter of the reactor is 2.957 m. This gives a cross sectional area ratio of 1.664. This keeps fluid velocity in the reactor unchanged.

Increasing the length of the reactor does not affect the conversion to urea. This means that the conversion is very close to equilibrium. The default kinetics of the simulation is relatively fast. We have the option to change the rate of reaction. In practice if we are far from equilibrium, we can increase the number of sieve plates in the reactor or use high efficiency trays.

Similar observations are noticed for a plant producing 1950 metric ton per day.

From Aspen Plus simulation, the following is the mole fractions of the liquid phase exiting the reactor,

\[ x_1=0.012175, \quad x_2=0.3492, \quad x_3=0.3272, \quad x_4=0.12175, \quad x_5=0.18851 \]

from which we can calculate

\(a=3.0017, b=0.4293\)

the exit temperature of the product from the reactor is 456 K.

Substituting these values in equations (3,13) we obtain

\[ K_i = 69.1 \]

\[ K_1 * K_2 = 41.19 \]

Whereas from the definition of the equilibrium constants, we have
This shows that the equilibrium constant (K1*K2) which expresses urea mole fraction at equilibrium conditions is accurately predicted. K1 which expresses carbamate mole fraction is less accurately predicted. In practice we are more concerned about urea concentration. Ammonia to CO₂ ratio in the recycle loop is in the range of 3. This means that ammonia is in excess. Large values for K1 indicate that most of CO₂ in the liquid phase is in the form of carbamate. Some investigators assume free CO₂ is 1% of total CO₂.

Another indicator is equilibrium conversion of equation (11) which gives a value of 0.6114. For the simulated plant this value is (0.18851/(0.18851+0.12175+0.012175)=0.5846)

IV CONCLUSION

In this paper empirical equations for the chemical equilibria for the reactions occurring in urea synthesis are obtained. Equation (13) can be used to check if equilibrium conversion of urea is approached. If equilibrium is not approached, we can think of increasing the sieve plates in the reactor or use high efficiency trays. In addition the equilibria constants are needed in the kinetic expression for carbamate and urea formation.

Knowledge of the carbamate concentration in different streams is also important since its formation is associated with the liberation of large amount of heat.

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Moustafa Aly Soliman, earned his bachelor’s and master’s degrees in chemical engineering from Cairo University; and his PhD in chemical engineering from the University of Waterloo. His pioneering research has resulted in three books, more than 170 journal and conference papers, and five patents.