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Urea Synthesis Reactor Modeling

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Abstract. In this work composition of ion and molecules are calculated using equilibrium relations of Urea synthetic reactions. This method is based on electrolyte system and considers all reactions of several species. To calculate deviation of liquid phase from ideal sate, the extended Deby-Hückel (E-DH) is used. The effects of N/C ratio and temperature changes were also studied.

Keywords: modelling, urea, synthesis, extended deby-hückel

1. Introduction

Calcium Cyanamide, H_2O, CO_2 and NH_3 will react to produce Urea. In second method that is very common and economical, NH_3 and H_2NCOO^- are combined in 3.5/1 inside the reactor in the range of temperature 180-210 ^{0}C and pressure 13-25 MPa. The reaction is performed in liquid phase and output mixture of reactor consist of urea, H2NCOONH4, Carbon Dioxide, unreacted NH_3 and H_2O [3-5].

2. Process Chemical Relations:

The following reaction displays the overall reaction of urea formation:

$$2NH_3(l) + CO_2(l) \Leftrightarrow NH_2CONH_2(l) + H_2O(l) \tag{1}$$

The synthetic reactor in which several ionic and molecular reactions take place cannot be accurately modeled using only the mentioned reaction.

The simulation has been also done by a number of researchers using the carbamate and urea equilibrium reactions which can be shown as:

$$2NH_3(l) + CO_2(l) \Leftrightarrow NH_2OCONH_4(l) \tag{2}$$

$$NH_2OCONH_4(l) \Leftrightarrow NH_2CONH_2(l) + H_2O(l) \tag{3}$$

According to the overall reaction the following ionic and molecular reaction can occur:

$$CO_2 + 2NH_3 \Leftrightarrow H_2NCOO^- + NH_4^+ \qquad K_4 = \frac{x_{NH_4^+} x_{H_2NCOO^-}}{x_{NH_3}^2 x_{CO_2}} \frac{\gamma_{NH_4^+} \gamma_{H_2NCOO^-}}{\gamma_{NH_3}^2 \gamma_{CO_2}}$$

$$CO_2 + NH_3 + H_2O \Leftrightarrow HCO_3^- + NH_4^+ \qquad K_5 = \frac{x_{NH_4^+} x_{HCO_3^-}}{x_{NH_3} x_{CO_2} x_{H_2O}} \frac{\gamma_{NH_4^+} \gamma_{HCO_3^-}}{\gamma_{NH_3} \gamma_{CO_2} \gamma_{H_2O}}$$

$$HCO_3^- + NH_3 \Leftrightarrow CO_3^{2-} + NH_4^+ \qquad K_6 = \frac{x_{NH_4^+} x_{CO_3^{2-}}}{x_{NH_3} x_{HCO_3^-}} \frac{\gamma_{NH_4^+} \gamma_{CO_3^{2-}}}{\gamma_{NH_3} \gamma_{HCO_3^-}}$$

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$$NH_3 + H_2O \Leftrightarrow HO^- + NH_4^+ \qquad K_7 = \frac{x_{NH_4^+} x_{OH^-}}{x_{NH_3} x_{H_2O}} \frac{\gamma_{NH_4^+} \gamma_{OH^-}}{\gamma_{NH_3} \gamma_{H_2O}}$$

$$H_2O \Leftrightarrow HO^- + H^+ \qquad K_8 = \frac{x_{H^+} x_{OH^-}}{x_{H_2O}} \frac{\gamma_{H^+} \gamma_{OH^-}}{\gamma_{H_2O}}$$

$$CO_2 + NH_3 \Leftrightarrow H_2NCOOH \qquad K_9 = \frac{x_{H_2NCOOH}}{x_{CO_2} x_{NH_3}} \frac{\gamma_{H_2NCOOH}}{\gamma_{CO_2} \gamma_{NH_3}}$$

$$H_2NCOO^- + NH_4^+ \Leftrightarrow H_2NCONH_2 + H_2O \qquad K_{10} = \frac{x_{H_2O} x_{H_2NCONH_2}}{x_{NH_4^+} x_{H_2NCOO^-}} \frac{\gamma_{H_2O} \gamma_{H_2NCONH_2}}{\gamma_{NH_4^+} \gamma_{H_2NCOO^-}}$$

$$x_{CO_2,in} = x_{CO_2} + x_{H_2NCOO^-} + x_{H_2NCOOH} + x_{H_2NCONH_2}$$

$$x_{NH_3,in} = x_{NH_3} + x_{H_2NCOO^-} + x_{H_2NCOOH} + x_{NH_4^+} + 2x_{H_2NCONH_2}$$

$$2x_{CO_2,in} = 2x_{CO_2} + 2x_{H_2NCOO^-} + 2x_{H_2NCOOH} + x_{H_2NCONH_2} + x_{H_2O} \qquad x_{NH_4^+} = x_{H_2NCOO^-}$$

To calculate the long range term of the activity coefficients, an electrolyte model such as extended Deby-Hückel (E-DH) or Pitzer model can be used. A common activity coefficient model such as NRTL, UNIFAC and UNIQUAC should be also applied to determine the short range term. Equations were combined to express the product ions and molecules concentrations, in terms of the CO_2 concentration[2,8,11,13].

$$2(x_{CO_2} + x_{H_2NCOO^-} + x_{H_2NCOOH} + x_{H_2NCONH_2}) = 2x_{CO_2} + 2x_{H_2NCOO^-} + 2x_{H_2NCOOH} + x_{H_2NCONH_2} + x_{H_2O} \Rightarrow x_{H_2NCONH_2} = x_{H_2O}$$

$$\frac{K_{10}\,\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}{\gamma_{H_2O}\gamma_{H_2NCONH_2}} = \frac{x_{H_2O} x_{H_2NCONH_2}}{x_{NH_4^+} x_{H_2NCOO^-}} = \frac{x_{H_2O}^2}{x_{NH_4^+}^2} \Rightarrow x_{H_2O} = x_{H_2NCONH_2} = x_{NH_4^+}\sqrt{\frac{K_{10}\,\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}{\gamma_{H_2O}\gamma_{H_2NCONH_2}}}$$

$$x_{NH_4^+} = x_{NH_3}\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}} x_{CO_2}} \qquad x_{H_2NCOOH} = \frac{K_9\,\gamma_{CO_2}\gamma_{NH_3}}{\gamma_{H_2NCOOH}} x_{CO_2} x_{NH_3}$$

$$x_{H_2O} = x_{Urea} = x_{NH_3}\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}} \frac{K_{10}\,\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}{\gamma_{H_2O}\gamma_{H_2NCONH_2}} x_{CO_2}}$$

$$x_{NH_3,in} = x_{NH_3} + 2x_{NH_3}\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}} x_{CO_2}} + \frac{K_9\,\gamma_{CO_2}\gamma_{NH_3}}{\gamma_{H_2NCOOH}} x_{CO_2} x_{NH_3}$$
$$+ 2x_{NH_3}\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}} \frac{K_{10}\,\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}{\gamma_{H_2O}\gamma_{H_2NCONH_2}} x_{CO_2}}$$

$$x_{NH_3} = 1 - x_{NH_3,in} + 2\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}x_{CO_2}} + \frac{K_9\,\gamma_{CO_2}\gamma_{NH_3}}{\gamma_{H_2NCOOH}}x_{CO_2}$$
$$+ 2\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}\,\frac{K_{10}\,\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}{\gamma_{H_2O}\gamma_{H_2NCONH_2}}x_{CO_2}}$$

Since the concentrations of the all species were expressed only in terms of x_{CO2}, the carbon balance can be used to calculate this unknown variable. In spite of the complexity of the thermodynamic study of the urea reactor, it can be easily modeled using only the following equation, developed in this work. To solve the equation ,Newton-Raphson method was applied[14-16]:

$$f = x_{CO_2} - x_{CO_2,in} + (1 - x_{NH_3,in} + 2\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}x_{CO_2}} + \frac{K_9\,\gamma_{CO_2}\gamma_{NH_3}}{\gamma_{H_2NCOOH}}x_{CO_2}$$
$$+ 2\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}\,\frac{K_{10}\,\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}{\gamma_{H_2O}\gamma_{H_2NCONH_2}}x_{CO_2}}\;)\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}x_{CO_2}}$$
$$+ \frac{K_9\,\gamma_{CO_2}\gamma_{NH_3}}{\gamma_{H_2NCOOH}}x_{CO_2}(1 - x_{NH_3,in} + 2\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}x_{CO_2}} + \frac{K_9\,\gamma_{CO_2}\gamma_{NH_3}}{\gamma_{H_2NCOOH}}x_{CO_2}$$
$$+ 2\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}\,\frac{K_{10}\,\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}{\gamma_{H_2O}\gamma_{H_2NCONH_2}}x_{CO_2}}\;)$$
$$+ (1 - x_{NH_3,in} + 2\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}x_{CO_2}} + \frac{K_9\,\gamma_{CO_2}\gamma_{NH_3}}{\gamma_{H_2NCOOH}}x_{CO_2}$$
$$+ 2\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}\,\frac{K_{10}\,\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}{\gamma_{H_2O}\gamma_{H_2NCONH_2}}x_{CO_2}}\;)\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}\,\frac{K_{10}\,\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}{\gamma_{H_2O}\gamma_{H_2NCONH_2}}x_{CO_2}}$$

$$f' = \left(\frac{-x_{NH_3,in}\left(\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}x_{CO_2}}} + \frac{K_9\,\gamma_{CO_2}\gamma_{NH_3}}{\gamma_{H_2NCOOH}} + \sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}\,\frac{K_{10}\,\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}{\gamma_{H_2O}\gamma_{H_2NCONH_2}x_{CO_2}}}\right)}{\left(1 + 2\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}x_{CO_2}} + \frac{K_9\,\gamma_{CO_2}\gamma_{NH_3}}{\gamma_{H_2NCOOH}}x_{CO_2} + 2\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}\,\frac{K_{10}\,\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}{\gamma_{H_2O}\gamma_{H_2NCONH_2}}x_{CO_2}}\right)^2}\right)$$
$$\left(\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}x_{CO_2}} + \frac{K_9\,\gamma_{CO_2}\gamma_{NH_3}}{\gamma_{H_2NCOOH}}x_{CO_2} + \sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}\,\frac{K_{10}\,\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}{\gamma_{H_2O}\gamma_{H_2NCONH_2}}x_{CO_2}}\right) +$$
$$\left(\frac{x_{NH_3,in}}{1 + 2\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}x_{CO_2}} + \frac{K_9\,\gamma_{CO_2}\gamma_{NH_3}}{\gamma_{H_2NCOOH}}x_{CO_2} + 2\sqrt{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}\,\frac{K_{10}\,\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}{\gamma_{H_2O}\gamma_{H_2NCONH_2}}x_{CO_2}}}\right)$$
$$\left(0.5\sqrt{\frac{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}}{x_{CO_2}}} + \frac{K_9\,\gamma_{CO_2}\gamma_{NH_3}}{\gamma_{H_2NCOOH}} + 0.5\sqrt{\frac{\frac{K_4\,\gamma_{NH_3}^2\gamma_{CO_2}}{\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}\,\frac{K_{10}\,\gamma_{NH_4^+}\gamma_{H_2NCOO^-}}{\gamma_{H_2O}\gamma_{H_2NCONH_2}}}{x_{CO_2}}}\right) + 1$$

3. Results and discussion:

To study the accuracy of the new algorithm, the industrial data were compared with the calculated ones, in table 1. The calculated mole fractions at various temperature and initial N/C molar ratios were presented in tables 2 and 3. The effects of these process parameters are also illustrated in figures 1 to 6[11,18].

Table 1: output results

	PFD values	Program output	Absolute deviation (%)
CO2	0.0466	0.0465	0.2983
NH3	0.6229	0.6227	0.0374
H2O	0.1652	0.1654	0.1550
Urea	0.1652	0.1654	0.1550

Table 2: the effect of outlet temperature at initial N/C=4.5

	Outlet temperature								
	160	170	180	190	200	210	220	230	240
CO_2	0.0506	0.0482	0.0465	0.0455	0.0453	0.0459	0.0472	0.0494	0.0521
NH_3	0.6287	0.6252	0.6227	0.6213	0.6210	0.6218	0.6238	0.6269	0.6309
Urea	0.1603	0.1633	0.1654	0.1666	0.1669	0.1662	0.1645	0.1619	0.1585
H_2O	0.1603	0.1633	0.1654	0.1666	0.1669	0.1662	0.1645	0.1619	0.1585

Table 3: the effect of initial N/C molar ratio @ 215o C

	Initial N/C molar ratio						
	3.9	4.1	4.3	4.5	4.7	4.9	5.1
CO_2	0.05893	0.054144	0.050027	0.046461	0.043352	0.040622	0.03821
NH_3	0.576332	0.592751	0.608179	0.622667	0.636268	0.64904	0.661038
Urea	0.182369	0.176553	0.170897	0.165436	0.16019	0.155169	0.150376
H_2O	0.182369	0.176553	0.170897	0.165436	0.16019	0.155169	0.150376

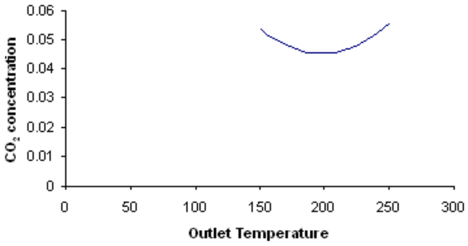

Fig. 1: the effect of outlet temperature on the CO_2 concentration at N/C=4.5

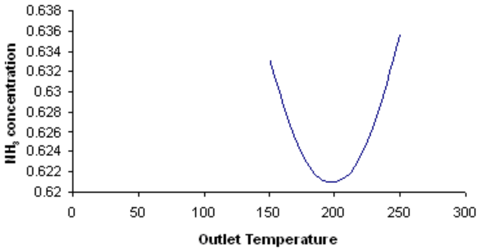

Fig. 2: the effect of outlet temperature on the NH3 concentration at N/C=4.5

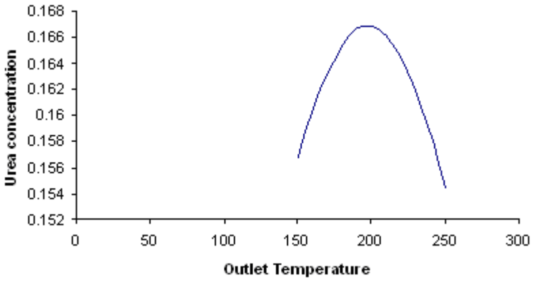

Fig. 3: the effect of outlet temperature on the Urea concentration at N/C=4.5

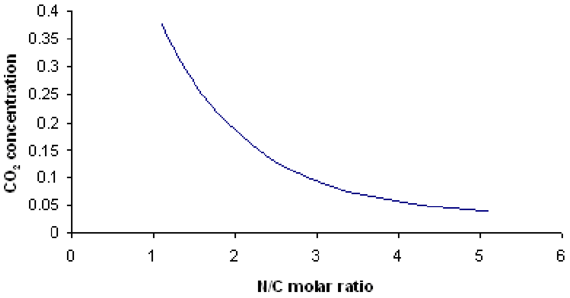

Fig. 4: the effect of initial N/C molar ratio on the CO_2 concentration at T=215°C

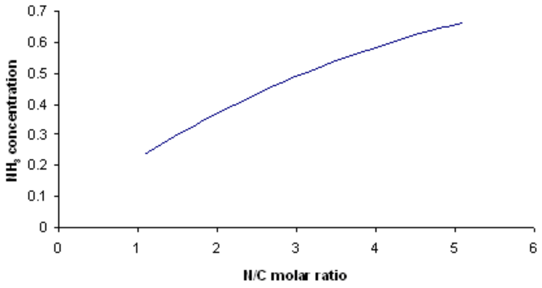

Fig. 5: the effect of initial N/C molar ratio on the NH$_3$ concentration at T=215^{o}C

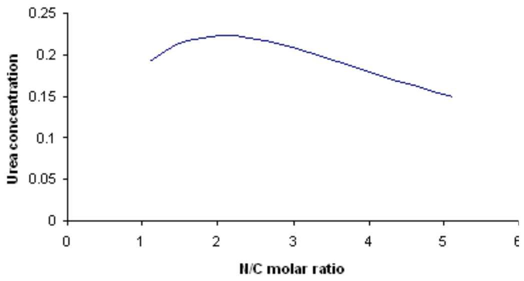

Fig. 6: the effect of initial N/C molar ratio on the Urea concentration at T=215^{o}C

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