International Journal of Engineering, Management and Humanities (IJEMH)
Volume 5, Issue 3, May.-June, 2024 pp: 194-202 ISSN: 2584-2145
www.ijemh.com

Optimization of Urea Yield by Ammonia Stripping Process

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Date of Submission: 12-06-2024 Date of Acceptance: 25-06-2024

UREA SYNTHESIS

NH_3&CO_2 react under specific concentration, temperature & pressure conditions to form Urea as per the following reactions:

$$CO_2\ (g) + 2NH_3\ (g) \longrightarrow NH_2COONH_4\ (s) \quad H = -37.64\ kcal/gmol$$

$$NH_2COONH_4\ (s) \longrightarrow NH_2CONH_2\ (s) + H_2O\ (l) \quad H=6.32\ kcal/gmol$$

$$CO_2\ (g) + 2NH_3\ (g) \longrightarrow NH_2CONH_2\ (s) + H_2O\ (l);\ H = -31.32\ kcal/gm\ mol$$

Therefore, overall urea synthesis is exothermic, releasing heat of 31.32 kcal/gm mol at standard conditions of 1 atm pressure & 25°C. However, actual heat available in a urea synthesis reaction will be only 5.74 kcal/gm mol because of the heat lost in evaporation of liquid NH_3, evaporation of water & melting of urea.

AMMONIA STRIPPING PROCESS

Formation of urea from ammonia & carbon-di-oxide takes place through reversible reactions with formation of ammonium carbamate as intermediate product. Now, success of any urea manufacturing process depends on how economically we can recycle carbamate to the reactor. AMMONIA STRIPPING PROCESS of urea manufacturing accomplishes the above task by stripping process.

$$NH_2COONH_4\ (s) \longrightarrow 2NH_3\ (g) + CO_2\ (g) \qquad H = +\ 37.4\ Kcal/gm\text{-}mole$$

This reaction involves increase in volume & absorption of heat. Thus, this reaction will be favored by decrease in pressure & increase in temperature. Moreover decreasing the partial pressure of either of the products will also favor the forward reaction. Process based on first principle of decrease in pressure & decrease in temp is called conventional process, whereas process based on increase/decrease of partial pressures of NH_3 or CO_2 is called stripping process.

According to above equation we have:

$$K = (pNH_3) * (pCO_2) \text{ [where, K= equilibrium constant]}$$

The stripping is effected at synthesis pressure itself using CO_2 or NH_3 as stripping agent.
If CO_2 is selected, it is to be supplied to the decomposers/stripper as in Stamicarbon CO_2 stripping process. While if NH_3 is selected, it is to be obtained from the system itself because excess is present in the reactor as in Snam's process. CO_2 stripping is advantageous because introducing CO_2 increase pCO_2. So pNH_3 will be reduced to maintain P constant as $P = pCO_2 + pNH_3$. At a particular temperature, K is constant so when pNH_3 is reduced to keep K constant, carbamate will be reduced much faster by decomposition as pNH_3 appears in the equilibrium equation with a power of two. Selection

of first stage decomposition should be in such a way that min water evaporates because the recovered gases go along with the carbamate to reactor again & if water enters reactor, production will be affected adversely due to hydrolysis of urea. Therefore, stage wise decomposition of carbamate is done. Second consideration in favor of isobaric stripping is that higher carbamate recycle pressure results in condensation at higher temperature & that recovery in the form of low-pressure steam. This is why stage wise reduction in pressure is practiced.

1) Pressure Recovery.
2) Urea Purification & Low-Pressure Recovery.
3) Urea Concentration.
4) Urea Prilling.

MATERIAL BALANCE

Selected capacity	: 1,50,000 tons/year
No. of working days	: 300
Daily production	: 1,50,000/300 = 500 tons/day
Urea	: 20,833 kg/hr of 98 % purity
Composition of the final product:	
Urea	: 98 % (20,416.34 kg/hr)
Biuret	: 1% (20,833*0.01=208.33 kg/hr)
Water	: 1%(20,833*0.01=208.33 kg/hr)

MAIN REACTIONS:

1) $CO_2 + 2NH_3 \longrightarrow NH_2COONH_4$
(44) (17) (78)

2) $NH_2COONH_4 \longrightarrow NH_2CONH_2 + H_2O$
(78) (60) (18)

Overall reaction:

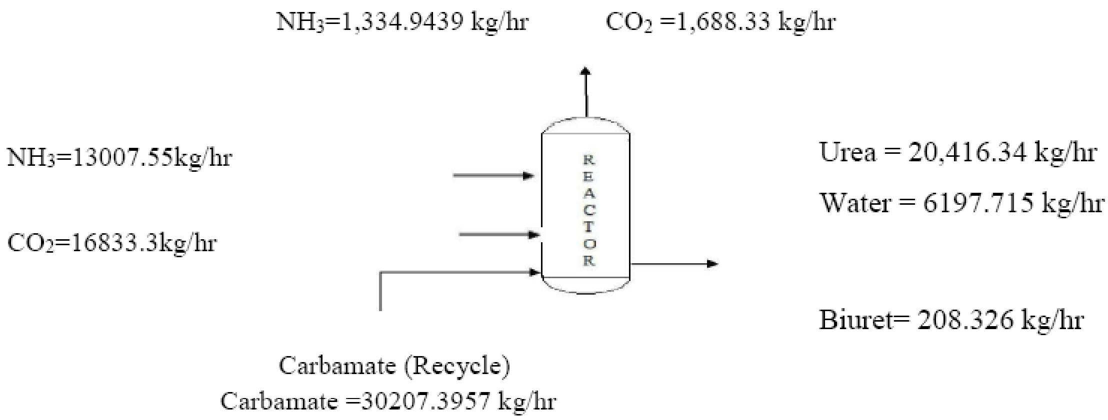
3) $CO_2 + 2NH_3 \longrightarrow NH_2CONH_2 + H_2O$
(44) (17) (60) (18)

Side reaction:

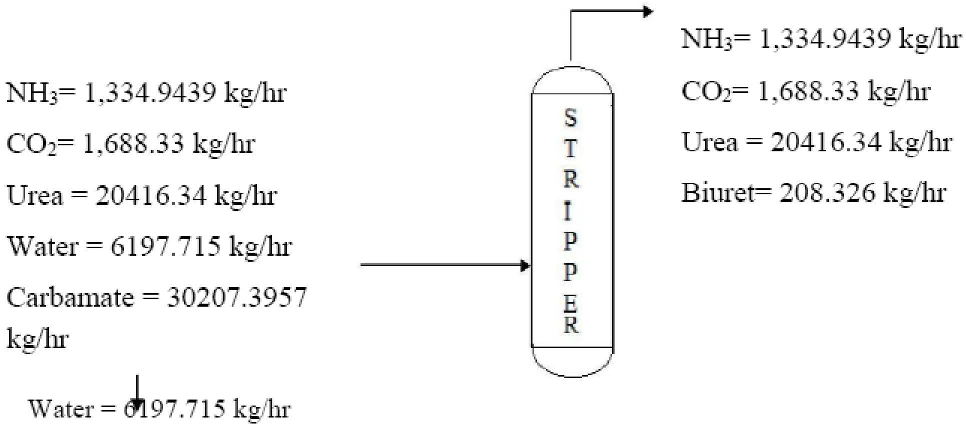
4) 2NHCONH $\longrightarrow$ NHCONHCONH + NH
(60) (103) (17) *From 4*

1kmol of CO_2 = 1 kmol of Urea
44 kg of CO_2 = 60 kg of Urea
To produce 20,659.05 kg/hr Urea= x kg/hr of CO_2 required
Similarly, CO_2reacted in reaction (1 or 3) = (44/60)* 20,659.05
= 15,149.97 kg/hr of CO_2
Now, Flow rate of carbamate = Flow rate of stream at reactor's exit – (flow rate of urea+CO_2+NH_3+water+biuret)
= 60,048.05-(20,416.34+1683.3+1334.9439+6197.715+208.326)
= 30207.3951 kg/hr

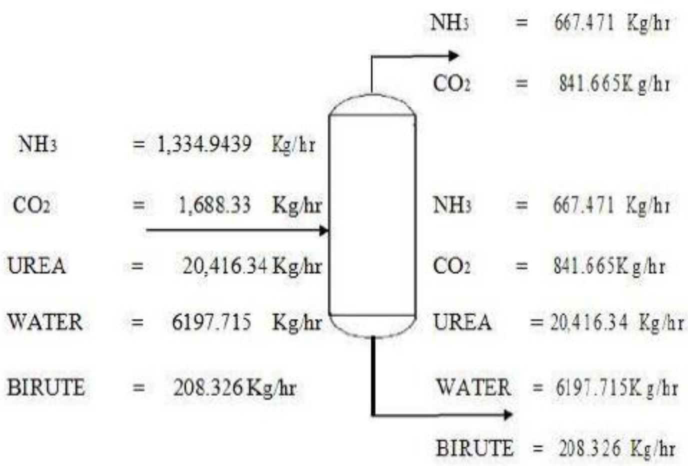
REACTOR



STRIPPER



MEDIUM PRESSURE SEPARATOR



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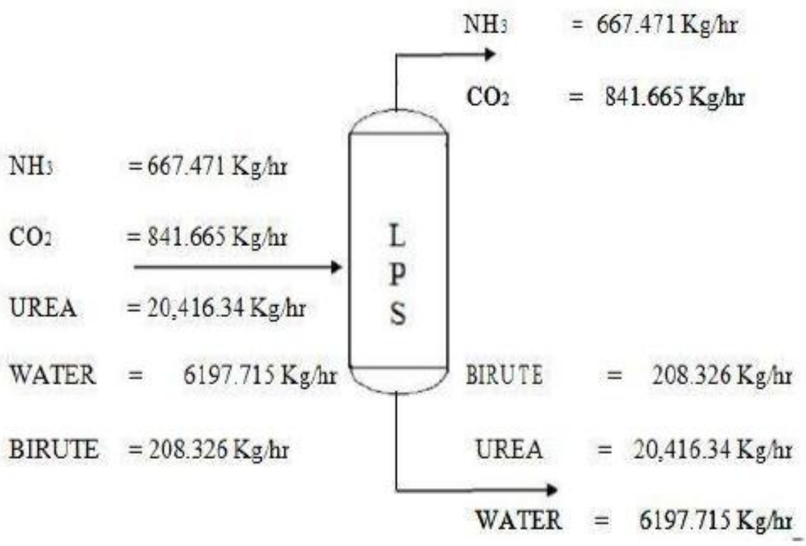
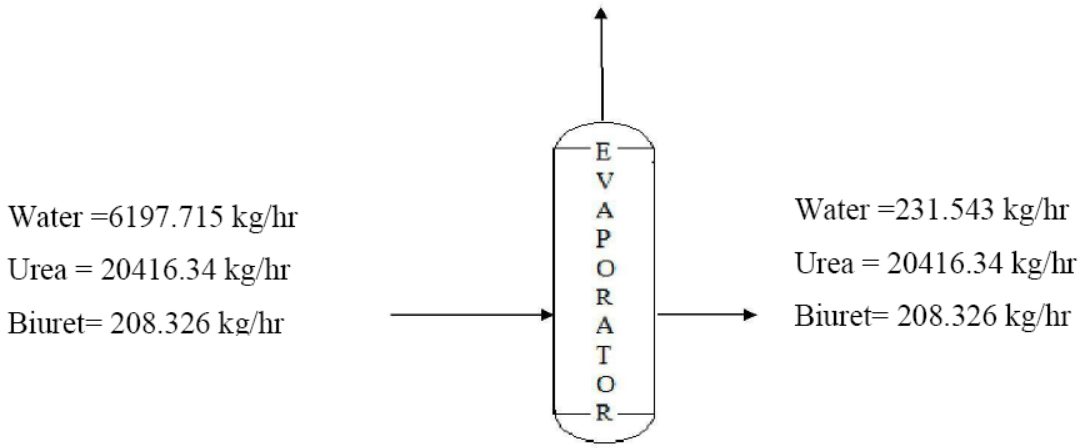
LOW PRESSURE SEPERATOR



VACUUM EVAPORATOR

Water = 5,965.572 kg/hr



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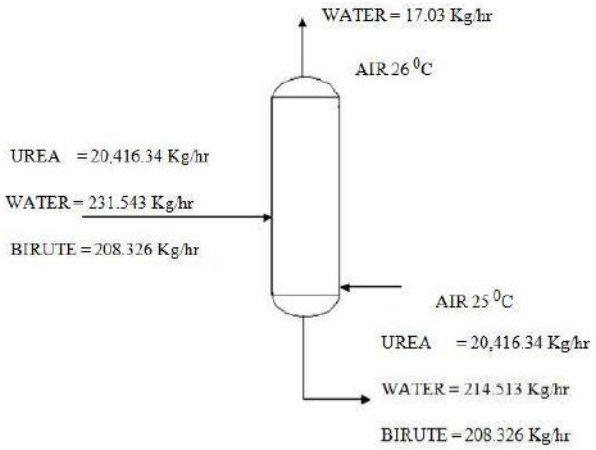
PRILLING TOWER



HEAT BALANCE

Evaporator :

Heat input (feed) + Heat input by steam = heat carried by water vapour + energy of the bottom product

Heat input (feed) + $S_1\lambda s_1$ = E_1HE_1 + energy of the bottom product

0.5029 x107 + S_1 x 2123.2 = 5965.572 x 2614.97 +0.3267 x 107

S_1=6517.42kg/hr

PRILLING TOWER

Heat input = 355.154 x 108.253 x 85 = 0.3267 x 10^7 kJ/hr

Flow of energy across prilling tower

Material	Specific heat at 30°C	Mol fractions (*x*)	Flow rate (kmol/l
Urea	0.3758 cal/gm °C = 94.41 kJ/kmol °C	0.9606	340.272
Water	1 cal/gm °C = 75.37 kJ/kmol °C	0.033	11.917
Biuret	0.308 cal/gm °C = 133.02 kJ/kmol °C	0.0057	2.022
	Total	1	354.211

C_p of mixture = $\sum x_iC_{pi}$

So, C_p = 0.96 x 94.41+0.033 x 75.37 + 0.0057 x 133.02 kJ/kmol C

= 93.879 kJ/kmol C

Heat output = 354.211 x 93.87 x 25 = 0.0831 x 107 kJ/hr

Assuming, humidity of air at 25 C = 0.01

Heat carried away by air = heat input – heat output (mC_pt) dry air = (0.3267- 0.0831) x 10^7

m = 0.2436*10 / (1+0.01) (1.009*25) flow rate of air,

m = 95614.71 kg/hr

DESIGN

DESIGN OF EVAPORATOR

Vapour space pressure = 0.23 atm

Vapour space temperature = 63.1°C, BPR =21.9°C

[Ref : Kirk Othmer, Encyclopedia of chemical technology,Vol-21]

Boiling point of liquid = 85°C

For product stream coming out of evaporator

Material	Specific heat at 30°C	Mol fractions (*x*)	Flow rate (kmol/
Urea	0.435cal/gm °C=109.28 kJ/kmol °C	0.9580	340.272
Water	1 cal/gm °C= 75.37 kJ/kmol °C	0.0362	12.86
Biuret	149 kJ/kmol °C	0.0056	2.0225
		1	355.154

C_p of mixture = $\sum x_iCp_i$

So, C_p = 0.958 x 109.28 + 0.0362 x 75.37 + 0.0056 x149kJ/kmol °C

= 108.253 kJ/kmol °C

$mC_p\Delta t = 0.3267 \times 10^7$ kJ/h

Heat Balance

Heat input (feed) + Heat input by steam = heat carried by water vapour + energy of the bottom product

Heat input (feed) + $S_1 \lambda_{s1} = E_1H_{E1}$ + energy of the bottom product

For steam at 147.165 °C, λ_{s1} = 2123.2 kJ/kg

Putting the values we get

$0.5029 \times 10^7 + S_1 \times 2123.2 = 5965.572 \times 2614.97 + 0.3267 \times 10^7$

S_1 = 6517.42 kg/hr

Economy = 5965.572/651742 = 0.9153

Now,

U_1 value is obtained from fig 5.0.1. At 63.1°C (145.58°F) the value of U1 is 270 Btu/hr.sq.ft.°F.

Multiplying this value by 5.6783 gives the value of U_1 in W/m^2K.

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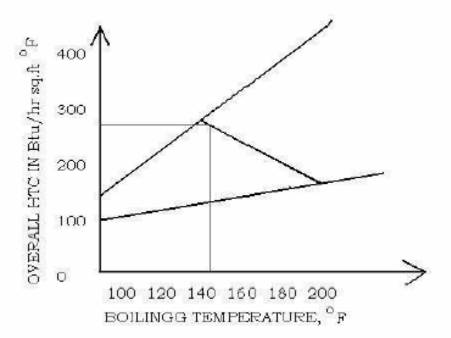
$A_1 = S_1 \lambda s_1 / U_1 T_1$ $T_1 = (\Delta T)app - BPR_1$

$= 147.165 - 63.1 - 21.9$

$= 62.165\ ^oC$

So, $A_1 = 6517.42 \times 2123.2 / 1533.141 \times 62.165 = 145.1906\ m^2$

(Ref: values of U_1 from Perry's handbook,10-35)



Graph to find out heat transfer co-efficient

$N_t = A/(\pi*OD*L)$
$N_t = 145.1906/(3.14*0.04*2)$
$N_t = 642$ tubes.
Total flow area = $\pi/4(ID)^2*N_t = (3.14*(0.036^2)*642)/4$
$= 0.65\ m^2$
Dia of downtake = $(0.5*(ID^2)*N_t)^{0.5} = (0.5*(0.036^2)*642)^{0.5}$
$= 0.65$ m
Area of downtake = $\pi/4(D_w)^2 = (3.14*(0.65^2))/4 = 0.33\ m^2$
Tube sheet area = Area of downtake+$(N_t*(P_t)^2) = 0.33+(642*(0.05^2))$
$= 1.935\ m^2$
Area of evaporator = 1.1*tube sheet area = 1.1*1.935=2.13 m^2

Dia of evaporator = $((A_e*4)/\pi)^{0.5}$=1.65m

Wall Thickness Calculation

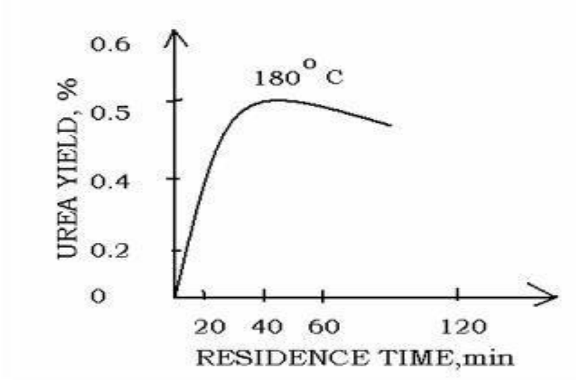
Material of construction : Mild steel $f = 0.93 \times 10^8\ N/m^2$, J =1.0 (perfectly welded)
$t = PD_i/(2fJ - P)$
Where, t = thickness of the shell
D_i = internal diameter
J = joint efficiency
P= design pressure
f = permissible stress
P = 1.1 x Ps
Ps= 4.5 atm = 4.413 bar $P = 4.854 \times 10^5\ N/m^2$
$t = (4.854 \times 10^5 \times 1.65) / (2 \times 0.93 \times 10^8 \times 1.0 - 4.854 \times 10^5)$
t= 5.08 mm

Design summary-Evaporator

S.NO	DESIGN PARAMETERS	VALUES/UNIT
1	AREA	145.1906 m^2
2	NO.OF.TUBES	642 TUBES
3	TUBE SHEET AREA	1.935 m^2
4	DIAMETER OF EVAPORATOR	1.65 m
5	HEIGHT OF EVAPORATOR	6 m
6	H/D RATIO	3.64
7	THICKNESS OF THE WALL	5.08 mm

DESIGN OF REACTOR

For the reaction to carryout plug flow reactor is choosen for high conversion



Yield vs Residence time plot for urea production

t = V/F

Where, t = residence time

F = Volumetric flow rate into the reactor in m^3/hr.

V = Volume of the reactor in m^3.

Density of liquid NH_3 = 618 Kg/ m^3

Density of CO_2 gas at 40 °C = 277.38 Kg/ m^3 (density=PM/RT) where p = 162atm,

T = 313K, R = 0.08206 L.atm/mol.K, M = 44g/mol

Density of Carbamate = 1600 Kg/ m^3

NH_3 flowing into the reactor = 13007.55/618 = 21.05 m^3/hr

CO_2 flowing into the reactor = 16833.33/277.5 = 60 m^3/hr

Carbamate flowing into the reactor = 30207.39/1600 = 18.87 m^3/hr

Total flow rate into the reactor = 21.05+60.00+18.87 = 99.93 m^3/hr

Residence time from the plot for 50% yield = 40 mins

t= V/F where V= volume of the reactor & F= total flow rate into the reactor

V = t*F = (40*100)/60 = 66.62 m^3

For plug flow reactor (L/D) ratio = 40.

$\pi/4*D^2*L = V$

For L=40D, $\pi/4*D^2*40D = 66.62$

D=1.28m, L=51.2m

Thickness Of The Shell

$t=PD_i/(2fJ-P)$

Material of construction-low alloy carbon (allowable stress =$1.18*10^8$ N/ m^2)

Internal pressure=162 atm=16200000 N/ m^2

Design pressure = $1.1*1.62*10^7 = 1.782*10^7$ N/ m^2 J = 1(perfectly welded)

$t = (1.782*10^7 *1.28)/(2*1.8*10^8 *1-(1.782*10^7))$ t = 67mm

Head Design
For Ellipsoidal head, $t = PD/(2fJ)$
$t = 1.716*10^7 *1.28/(2*1.8*10^8*1)$
t = 61mm

Design summary- Reactor

S.NO	DESIGN PARAMETERS	VALUES/UNIT
1	VOLUME	66.62 m3
2	LENGTH	51.1m
3	DIAMETER	1.28m
4	THICKNESS OF THE SHELL	67mm
5	HEAD CHOOSEN	ELLIPSOIDAL
6	THICKNESS OF HEAD	61mm

CONCLUSIONS

The selected capacity of the plant is 1,50,000 tons/year based on 300 working days. The product from the prilling tower contains 98 % urea. Critical review of all the manufacturing processes has been presented. Ammonia Stripping Process has been selected for the project. The ammonia-stripping urea process involves a high NH3 to CO2 ratio in the reactor, ensuring the high conversion of carbamate to urea. The highly efficient ammonia stripping operation drastically reduces the recycling of carbamate and the size of equipment in the carbamate decomposition. Snamprogetti technology differs from competitors in being based on the use of excess ammonia to avoid corrosion as well as promote the decomposition of unconverted carbamate into urea. Material & energy balance for each of the equipment has been done. Climbing-film, long tube vertical evaporator is used for the concentration of urea and plug flow reactor is used as a reactor.