

Urea

\* Mol. formula  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH}_2$ . It contains  
46.5 w.t% N<sub>2</sub>.

\* M.P.  $132.6^\circ\text{C}$

\* Decomposes to  $\text{NH}_3$  & carbonic acid



\* Fairly soluble in water. (110 gm / 100 gm  
at  $20^\circ\text{C}$ )

Uses: Fertilizer, polymerisation  
for adhesive,  
formaldehyde resins

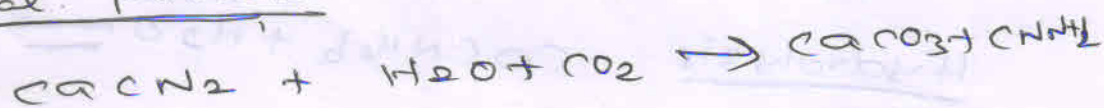
malamine formaldehyde resins.

\* controls NO<sub>x</sub>,  $\text{NO}_x + \text{urea} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

Chemistry

\* Our body produces 20-30 g urea/day

\* 1828. Wohler. Urea can be  
prepared from  $\text{NH}_3$  & carbonic acid, in  
aq. soln.

Initial process

After Haber's process in 1913,



$$\Delta H = -117 \text{ kJ/mol}$$

→ Fast exothermic



$$\Delta H = +15.5 \text{ kJ/mol}$$

slow & endothermic,

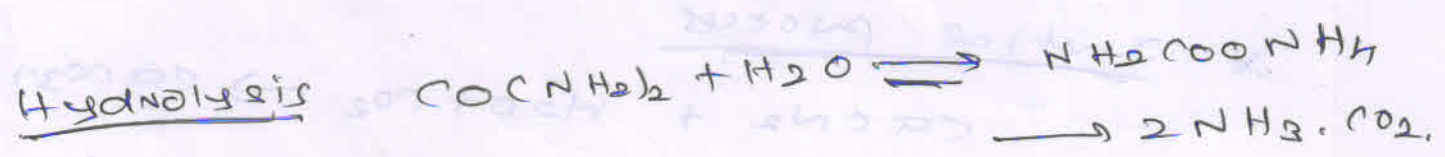
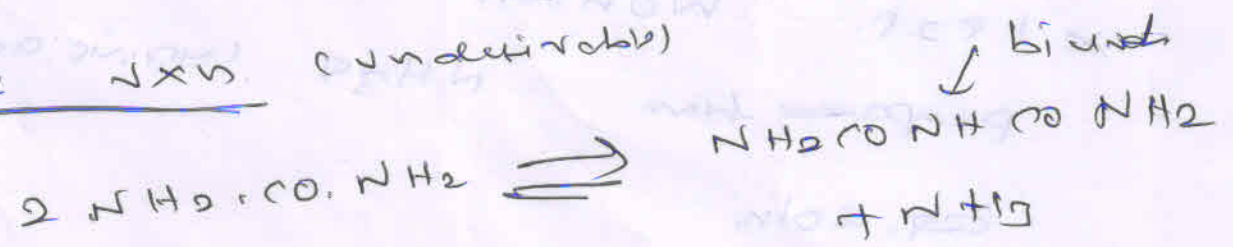
\* Over all process is exothermic.

\* First rxn goes to completion under the high pressure condition employed.

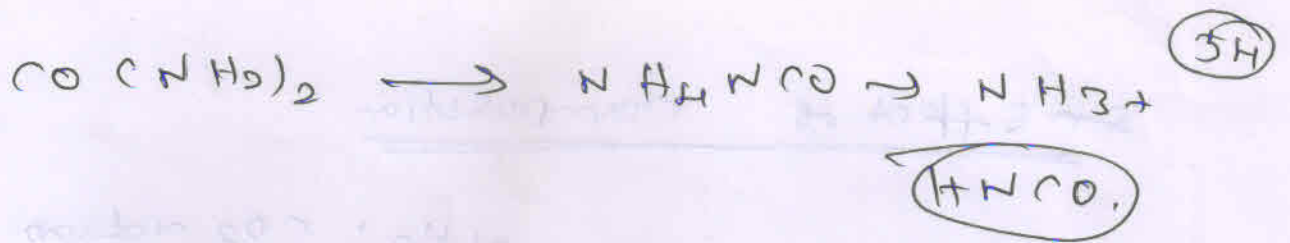
\* However, 2nd rxn does not go to complete.

\* Over all conversion (for  $\text{CO}_2$  both) is 50-80%.

Side rxn (undesirable)



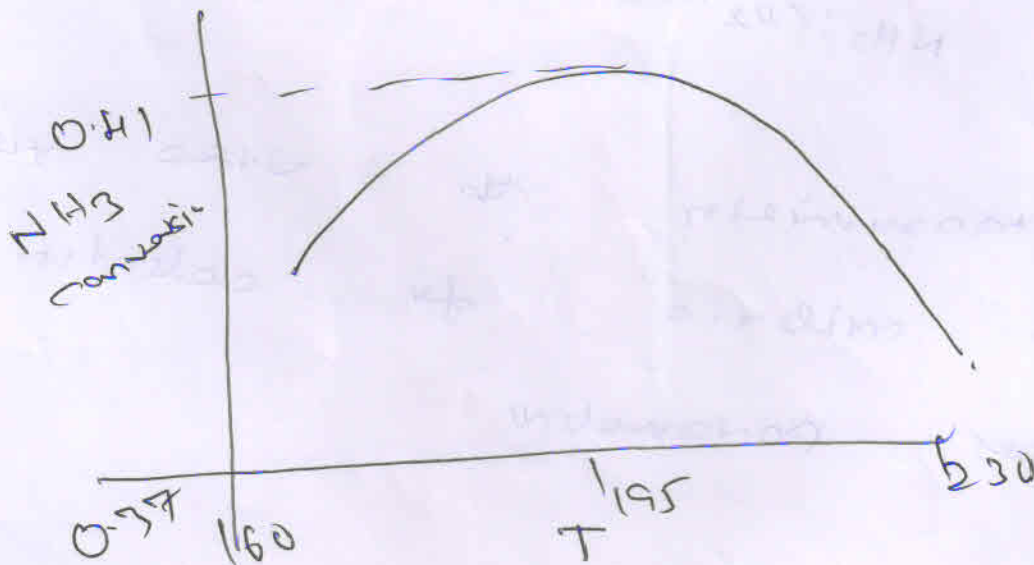
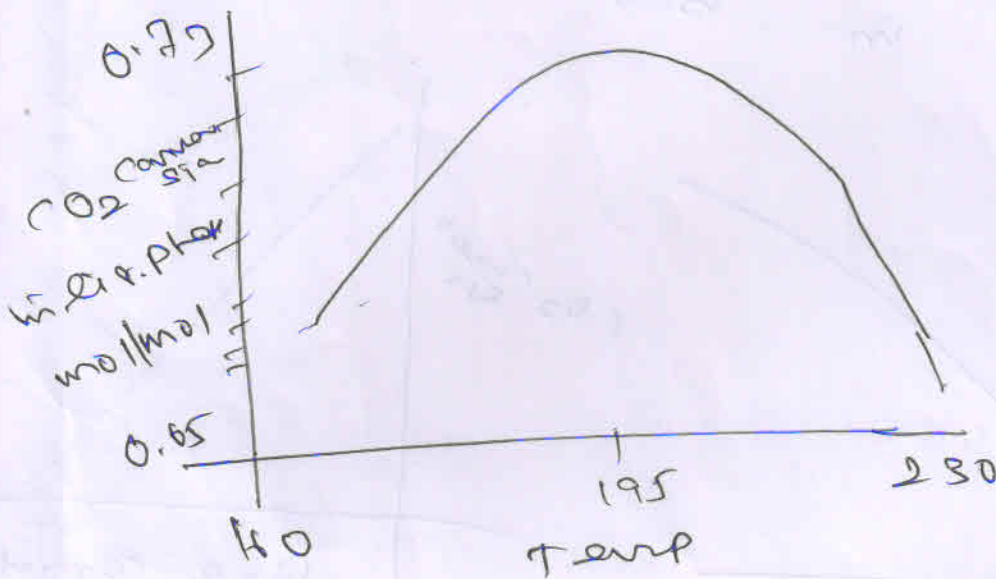
Form



Isocyanic acid

### Process

- \* Differ mainly in the condition in which  $\text{NH}_3$  and  $\text{CO}_2$  are mixed
- \*  $\text{NH}_3$  and  $\text{CO}_2$  are mixed in different proportions

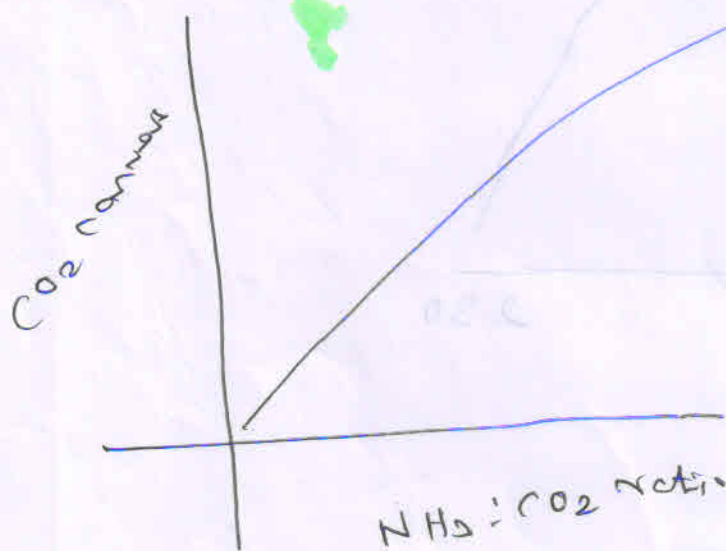




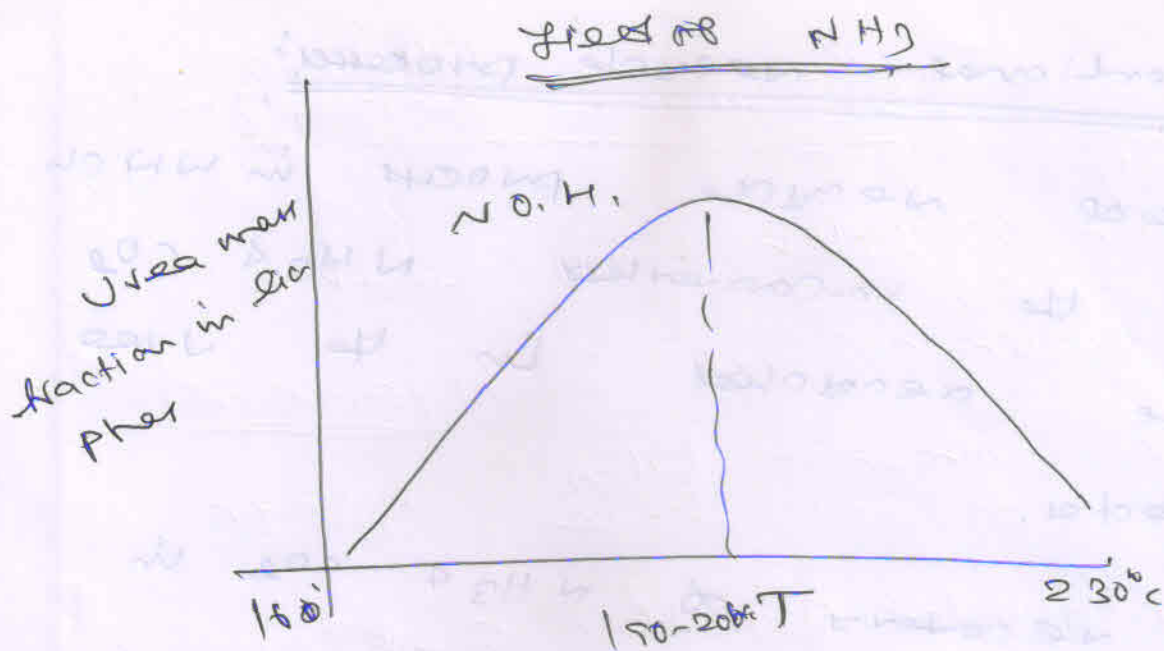
## Effect of Composition

① Increase the  $\text{NH}_3 : \text{CO}_2$  ratio  
increases  $\text{CO}_2$  conversion but  
reduces  $\text{NH}_3$  conversion

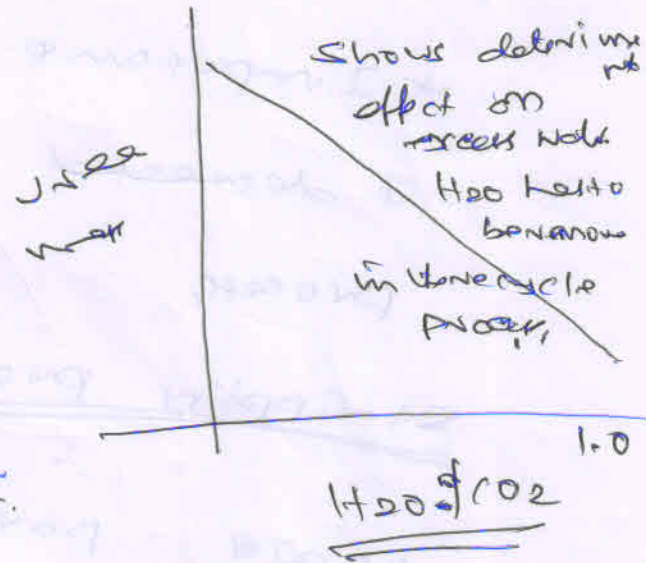
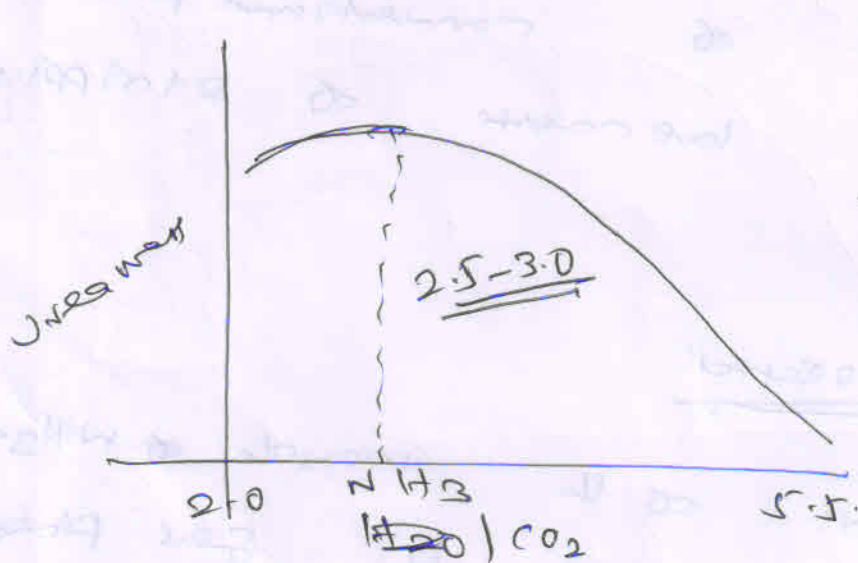
② Increase the amount of  $\text{H}_2\text{O}$  in  
the initial mixture ( $\uparrow$  in  $\text{H}_2\text{O} \% \text{CO}_2$ )  
decrease in both  $\text{CO}_2$  &  $\text{NH}_3$  conversion



For maximizing the urea yield  
right criteria for selection is  
process parameters



$\text{NH}_3 / \text{CO}_2 = 3.5 \text{ mol/mol}$   $\text{H}_2\text{O} / \text{CO}_2 = 0.25 \text{ mol/mol}$



Types of process:

Once through process:

$\text{NH}_3$  was neutralized with acid (e.g.  $\text{HNO}_3$ ) to produce ammonium salts.

Disadv: Large amt of ~~ammonium salts~~ as co-product & limited range of  $\text{CO}_2$ .

## Conventional recycle process:

TOTAL recycle process in which  
all the un-converted  $\text{NH}_3$  &  $\text{CO}_2$   
were recycled in the next  
reactor.

→ recycle of  $\text{NH}_3$  &  $\text{CO}_2$  in  
2 stages.

\* Importance of conventional process  
of domestic  
process because of stripping

## stripping process:

Major part of the recycle of  $\text{NH}_3$   
 $\text{CO}_2$  occurs via the gas phase.  
4 minimized water recycle to the  
both reactors.



# Stripping process → pool reactor

(56)

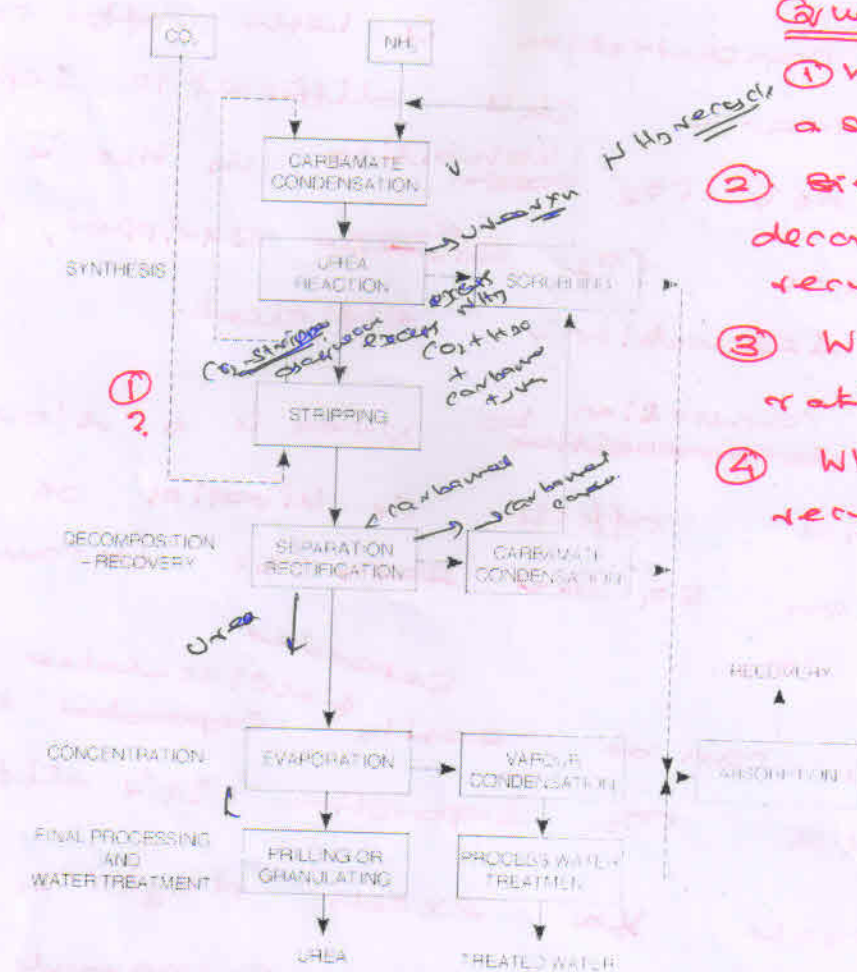
Questions:

① Why  $\text{CO}_2$  is passed through a stripper?

② Why carbamate is decomposed to  $\text{NH}_3$  &  $\text{CO}_2$  and recycled? enhanced

③ Why  $2\text{NH}_3 : \text{CO}_2$  ratio is preferred?

④ Why do we need two recycle process?



Urea plant block diagram. Conventional process

\* All  $\text{CO}_2$  unconverted  $\text{NH}_3$  &  $\text{CO}_2$  is recycled

\* There are two recirculation stages.

\* One first is operated at medium pressure (18-25 bar). and at 2-5 bar.

\* First recirculation stage comprises:

① Decomposition heater → decomposes carbamate to give  $\text{NH}_3$  &  $\text{CO}_2$

② The off gas  $\text{NH}_3$  from is separated & unreacted  $\text{aq. NH}_3$  ammonium carbamate is recycled separately

③  $\text{CO}_2$  is recycled as  $\text{CO}_2$  aqueous &  $\text{NH}_3$  is an aqueous

④ operates at high  $\text{NH}_3 : \text{CO}_2$  ratios (4-5).

## Answers for Questions?

- ① Since  $\text{CO}_2$  concentration is lower after coming out of urea reactor it is difficult to separate as aq. soln. (Note:  $\text{CO}_2$  solubility in  $\text{H}_2\text{O}$  is high). If  $\text{CO}_2$  is sent to  $\text{CO}_2$  stripper, solubility will be lower & separation is efficient.
- ② Carbamate <sup>conversion to</sup> ~~decomposition~~ urea is a slow reaction & its accumulation affects the kinetics of the first reaction. So, it is easy to decompose and to  $\text{NH}_3$  &  $\text{CO}_2$ .
- ③ Excess  $\text{NH}_3$  can be <sup>separated</sup> easily <sup>& recirculates</sup> ~~separated~~ as  $\text{NH}_3$ . Instead of  $\text{CO}_2$  separation (It is difficult)
- ④ First recycle for excess  $\text{NH}_3$  &  $\text{CO}_2$ .  
Second recycle for the excess carbamate formation.



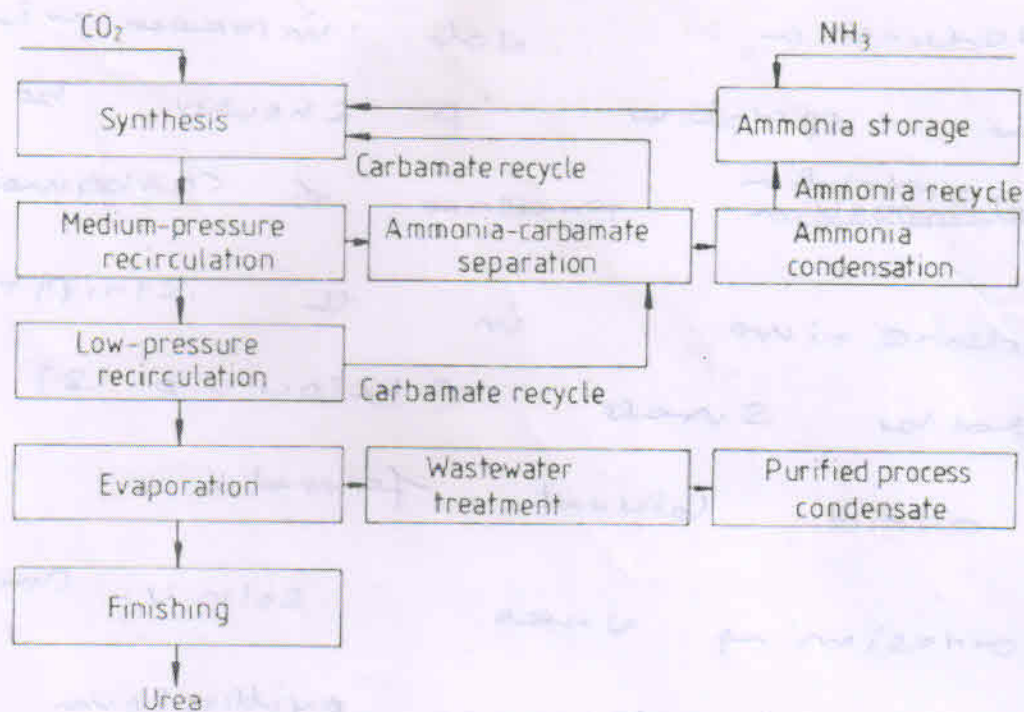


Figure 24. Functional block diagram of the Snamprogetti self-stripping process

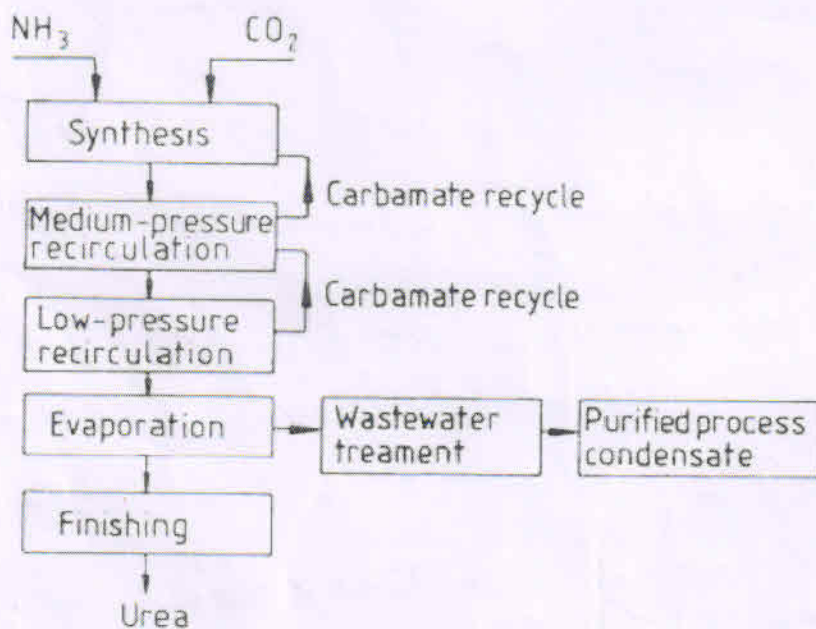


Figure 26. Functional block diagram of the ACES urea process

## Major engineering problems:

- ① Production rate increases with pressure. operation P should be above the <sup>association</sup> ~~dissociation~~ pressure of carbonates
- ② Residence time in the stripping column should be small (below 1-2 s) because to avoid binder formation
- ③ Corrosion → uses solvent corrosive
- ④ Binder formation in reboiler tower