# UREA PLANT

# Introduction

- Urea (identified 1773), the first organic compound prepared by inorganic synthesis (1828 Wohler)

$$NH_3 + HCNO \rightarrow CO(NH_2)_2$$

- Commercial production started in 1922 – Germany, 1932 – USA and 1935 – UK.
- Urea has been considered as slow – release fertilizer since it must undergo two transportation
  1. Hydrolysis: $CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$
  2. Nitrification: $NH_3 \rightarrow$ Nitrite or Nitrate (Microbes, moist and warm soil )
- Biuret is the impurity in urea.
- More than 50 M tons is produced annually

# Uses of Urea

- Main $N_2$ fertilizer, specially for the flooded region.
- Cattle feed supplement where it is cheap.
- Feed material for melamine plastics and various glues (Urea – Formaldehye, urea – melamine – formaldehyde)
- Use: Prill or microprill (0.2-0.4 mm), liquid mixture of urea (±75% solution), molasses, phosphoric acid.

# Properties of Urea

| | |
|---|---|
| Molecular weight | 60.06 |
| $N_2$ Content, % | 46.6 |
| Color | White |
| Specific gravity | 1.335 |
| Melting point $^oC$ | 132.7 |
| Critical relative humidity<br>20$^oC$<br>30$^oC$ | <br>81%<br>73% |
| Specific heat 20$^oC$, Cal/g$^oC$ | 0.32 |
| Heat of solution in water (endothermic) Cal/g$^oC$ | -57.8 |

# Process Operating Variables

## Reactions:

$$2NH_3 + CO_2 \rightarrow H_2NCOONH_4$$

$$H_2NCOONH_4 \rightarrow H_2NCONH_2 + H_2O$$

## Temperature:

- Rate of Carbamate decomposition reaction increases with temperature. It is slow at < 150°C ($NH_3$:$CO_2$, stoichiometric) and quite rapid at 210°C.
- 180-210 °C in 0.3 to 1.0 hr is optimum for most process. At high temperature, corrosion rate is high.

## Pressure:

- Preferred pressure is 140 – 250 atm.

## Mole ratio of $NH_3$: $CO_2$

- Excess ammonia above the stoichiometric ratio favors the rate of reaction. (3:1 = $NH_3$: $CO_2$)

## Other factors:

- The presence of water decreases conversion.
- The presence of small amount of $O_2$, decreases corrosion.

# Optimum Conditions

- Maximize the production of urea per unit time with due regard to cost of recycling unreacted $NH_3$ and $CO_2$, the cost increase of reactor size, corrosion difficulties. NOT to increase the percentage of conversion.

## Typical Operating Conditions:

T: 180 – 210°C

$NH_3:CO_2$ = 3.1 - 4.1

P: 140 – 250 atm

Retention time: 20-30 min

# Urea Processes

- ❑ Once – Through
- ❑ Partial recycle
- ❑ Total recycle (All new plants)
  - Stamicarbon: ZFCL, KAFCO
  - Snamprogetti (Snam): JFCL
  - Mitsu – Toatsu (M – T): UFFL Before 1990.
  - Advanced Cost and Energy Saving (ACES) by TEC: UFFL (After 1990), CUFL

# Once Through Process

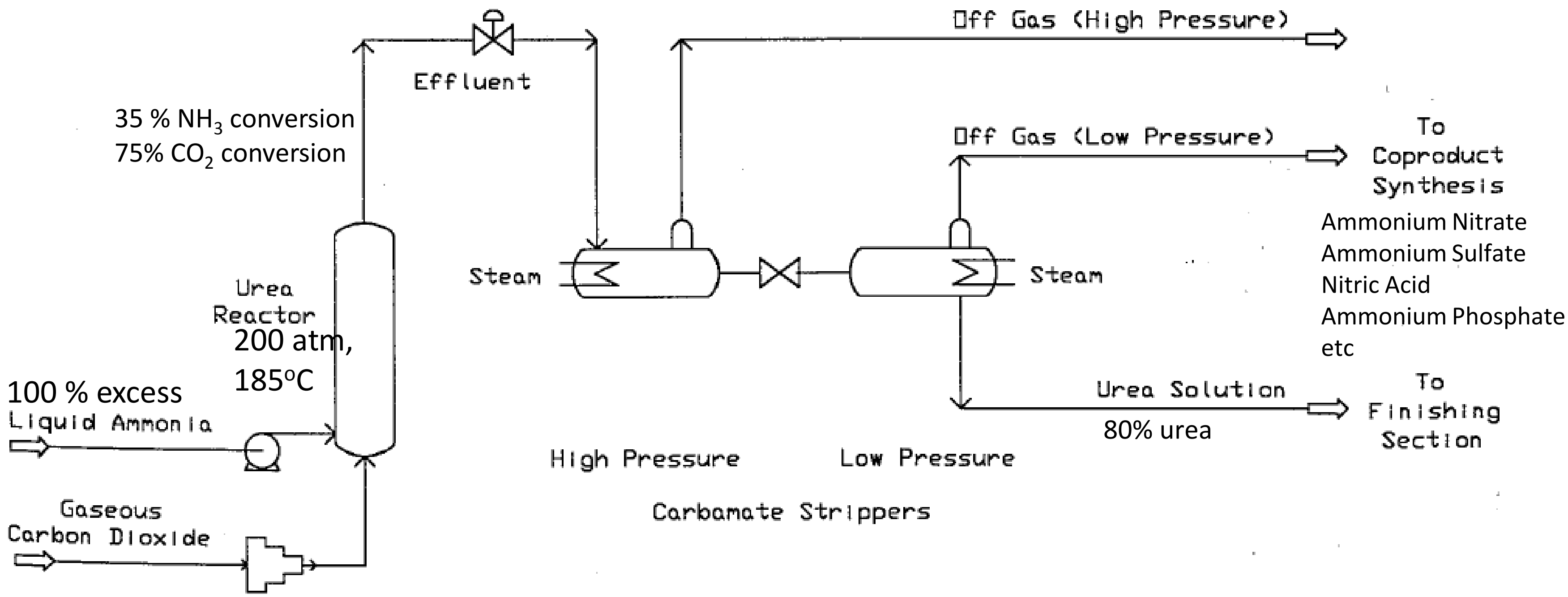



**Figure 9.1. Typical Once-Through Urea Process.**

- The once – through process is simplest and least expansive (both capital and operating cost) among the three process.
- Least flexible and cannot be operated unless some provision is made to utilize large amount of ammonia and off-gas.

# Partial Recycle Process

- Part of the off – gas is recycled back to the reactor.
- The amount of ammonia is reduced to 15% to that of once through that must be used in other processes.
- Investment cost is somewhat lower than the total recycle process, this advantage apparently does not compensate the inflexibility arising from the necessity to operate a co-product plant with mutual interdependency problems. However it finds application in UAN co-product plants.

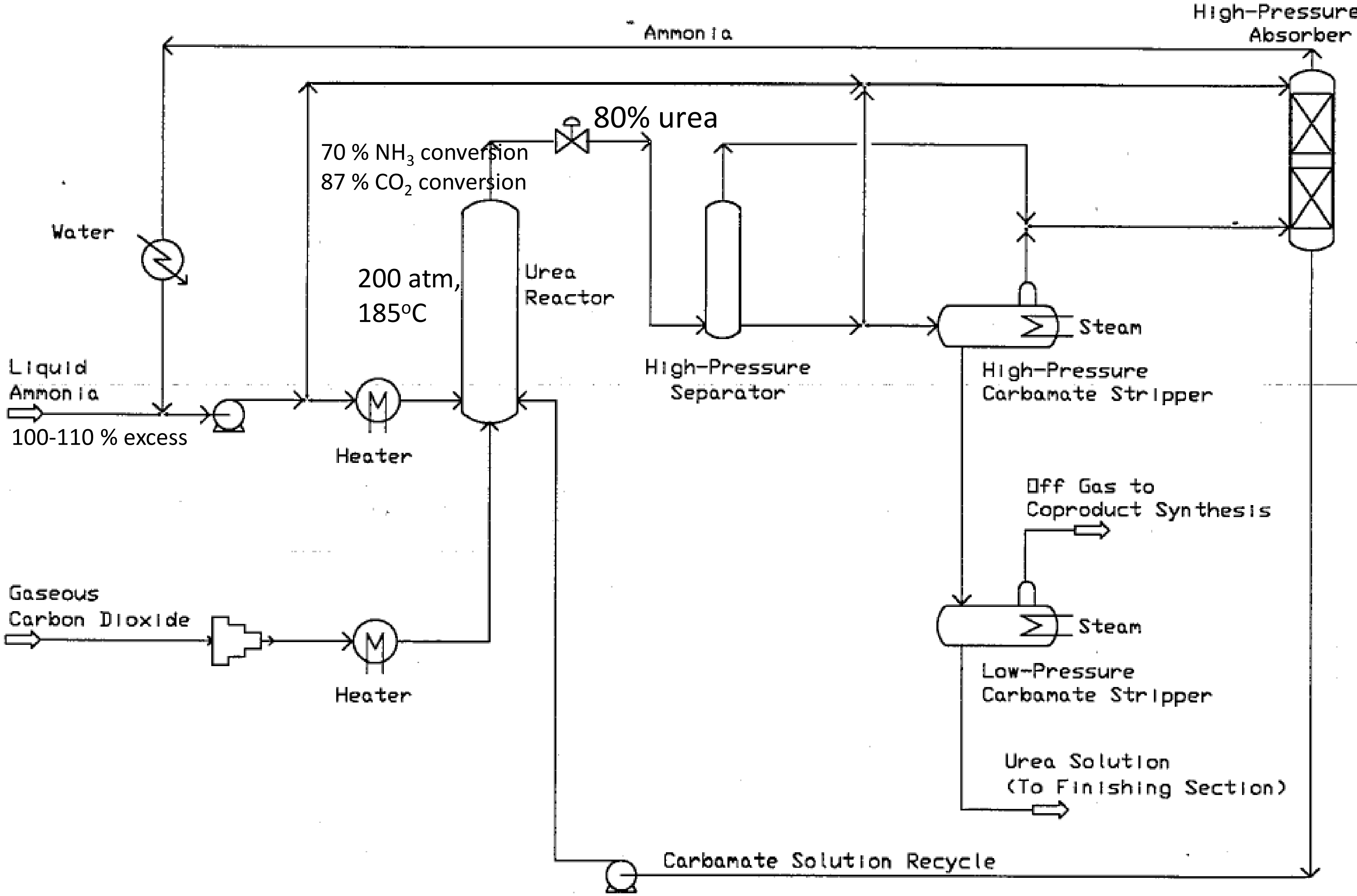



**Figure 9.2. Typical Partial-Recycle Process.** ( Mitsui – Toatsu )

# Total Recycle Processes

- All unconverted $NH_3$ and $CO_2$ is recycled back to the reactor (99% conversion).
- No nitrogen co-product is necessary.
- Most flexible urea process as it depends only $NH_3$ and $CO_2$ supply.
- Most expensive in investment and operating cost.

# Classification of Total recycle Processes

Reactor outlet contains UREA, $NH_3$, $CO_2$, $H_2O$, and CARBAMATE which must be decomposed before recycle.

$$NH_2CO_2NH_4 \rightleftarrows CO_2 + 2NH_3$$

- Hot – gas mixture recycle
- Separated gas recycle
- Slurry recycle
- Carbamate - solution recycle

(Carbamate Decomposition)

- Stripping → Modern Processes: Snam, Stamicarbon, ACES

The general design objectives are:

- Maximize the heat recovery
- Minimize the amount of carbamate solution recycled (smaller pumps and less power) and amount of water returned to the reactor (better conversion).
- Minimize power requirement
- Maximize ammonia recovery (lowering operating cost and less pollution)
- Other important requirement is of-course minimizing investment. The problem is finding the best balance between the utility consumption and maintenance on one hand and investment on the other hand.

# Urea Manufacturing Process

**Desired Reactions**

$2NH_3$ (liquid) + $CO_2$ (gas) = $NH_4COONH_4$ +38.06 Kcal/mol

$NH_4COONH_4$= $NH_2CONH_2$ + $H_2O$ -522 Kcal/mol

**Undesired Reaction**

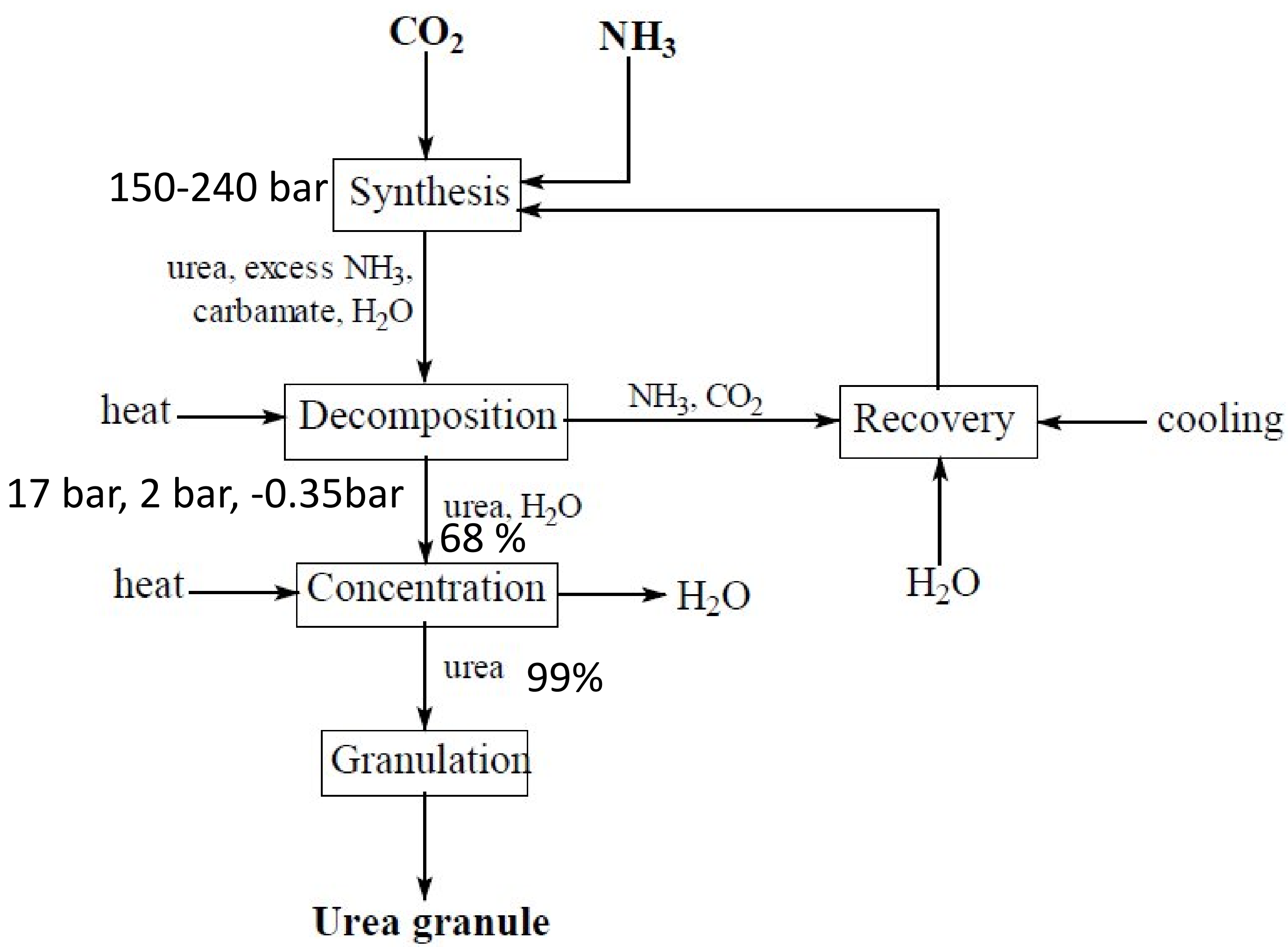
$$2NH_2CONH_2 \leftrightarrows \underset{\text{biuret}}{NH_2CONHCONH_2} + NH_3$$

Reduce yields of Urea,
Burns the leaves of plants

Three major design considerations:

- to separate the urea from other constituents,
- to recover excess $NH_3$ and
- decompose the carbamate for recycle.

# Block Diagram of Urea Synthesis



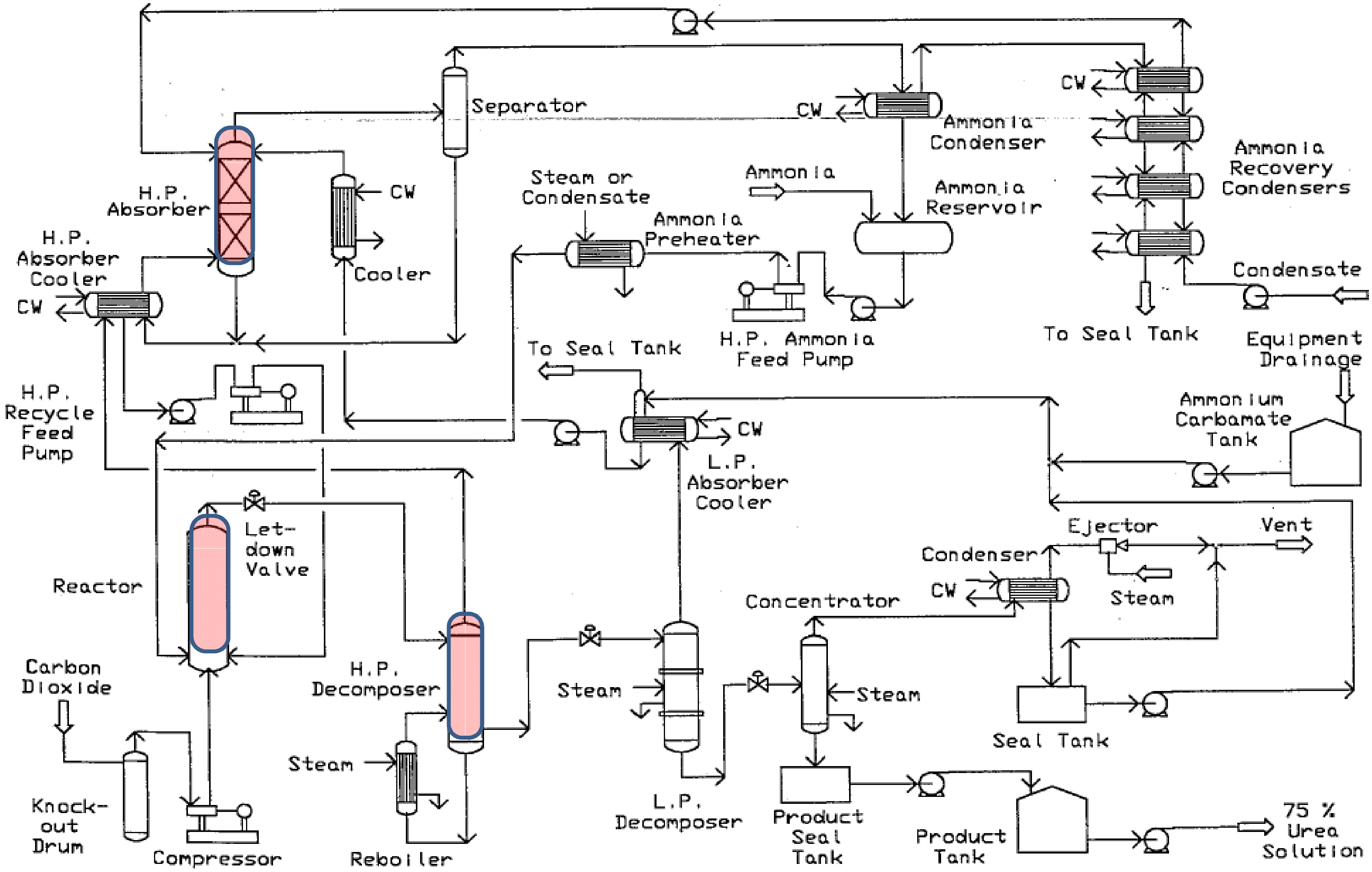



**Figure 9.3. Typical Total-Recycle Urea Process (TVA Plant).** (Mitsui – Toatsu)

# Stripping Process Based Plants

- In 1966 Stamicarbon of Netherland introduced $CO_2$ stripping → Snamprogetti built a plant using $NH_3$ as stripping process (requires high $NH_3:CO_2$ ratio) later switched to thermal stripping → Toyo Engineering Corpora on (TEC) Japan utilized $CO_2$ stripping.
- Three licensors have different approaches and have improved their technology throughout the years.
  - Closely stoichiometric amount of raw material consumption
  - Reduced steam consumption to an apparently economic level
  - Avenues available for improvements in reduction of capital cost, improved reliability and efficiency of mechanical improvements and advances in metallurgical advances.

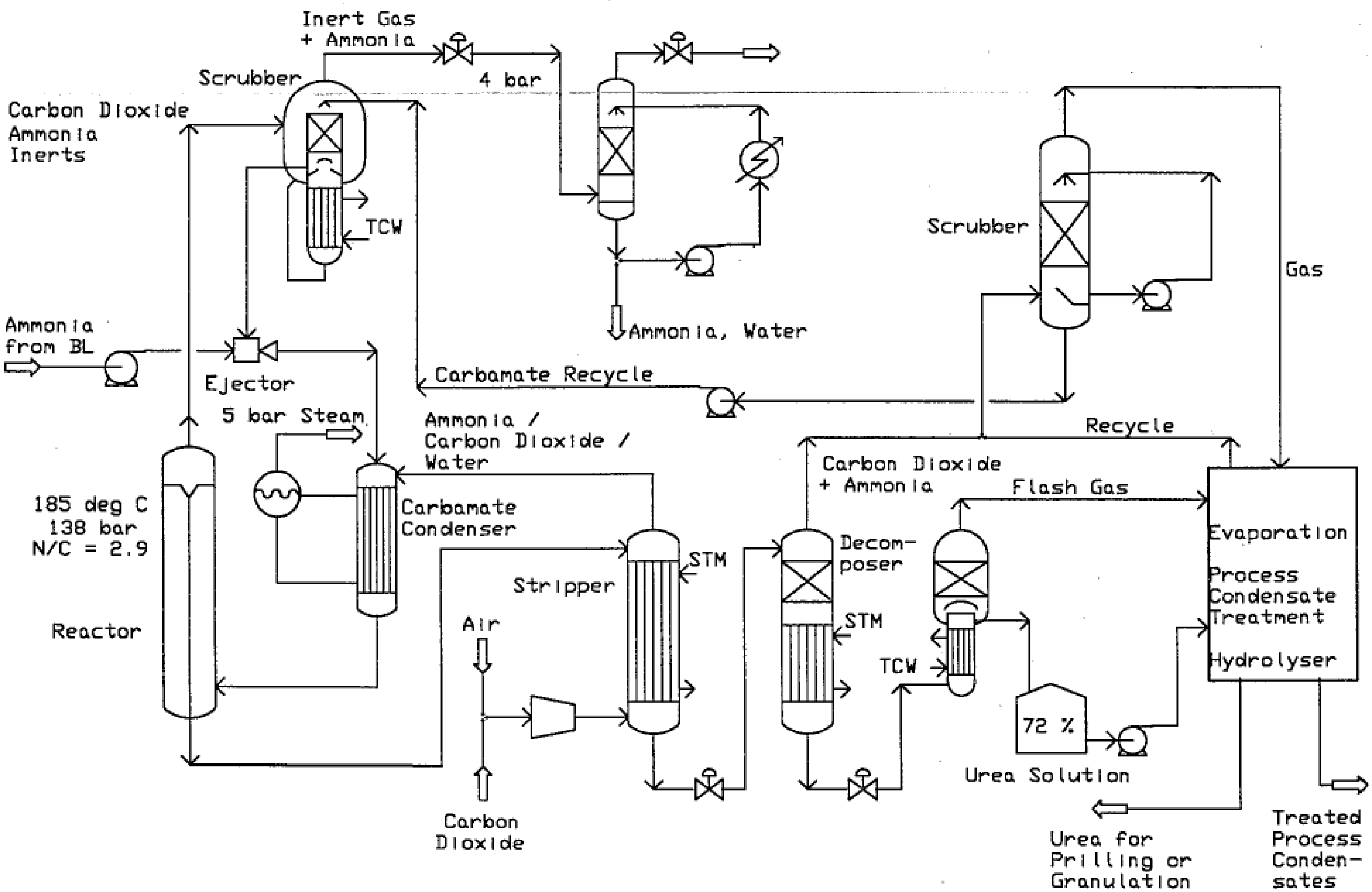
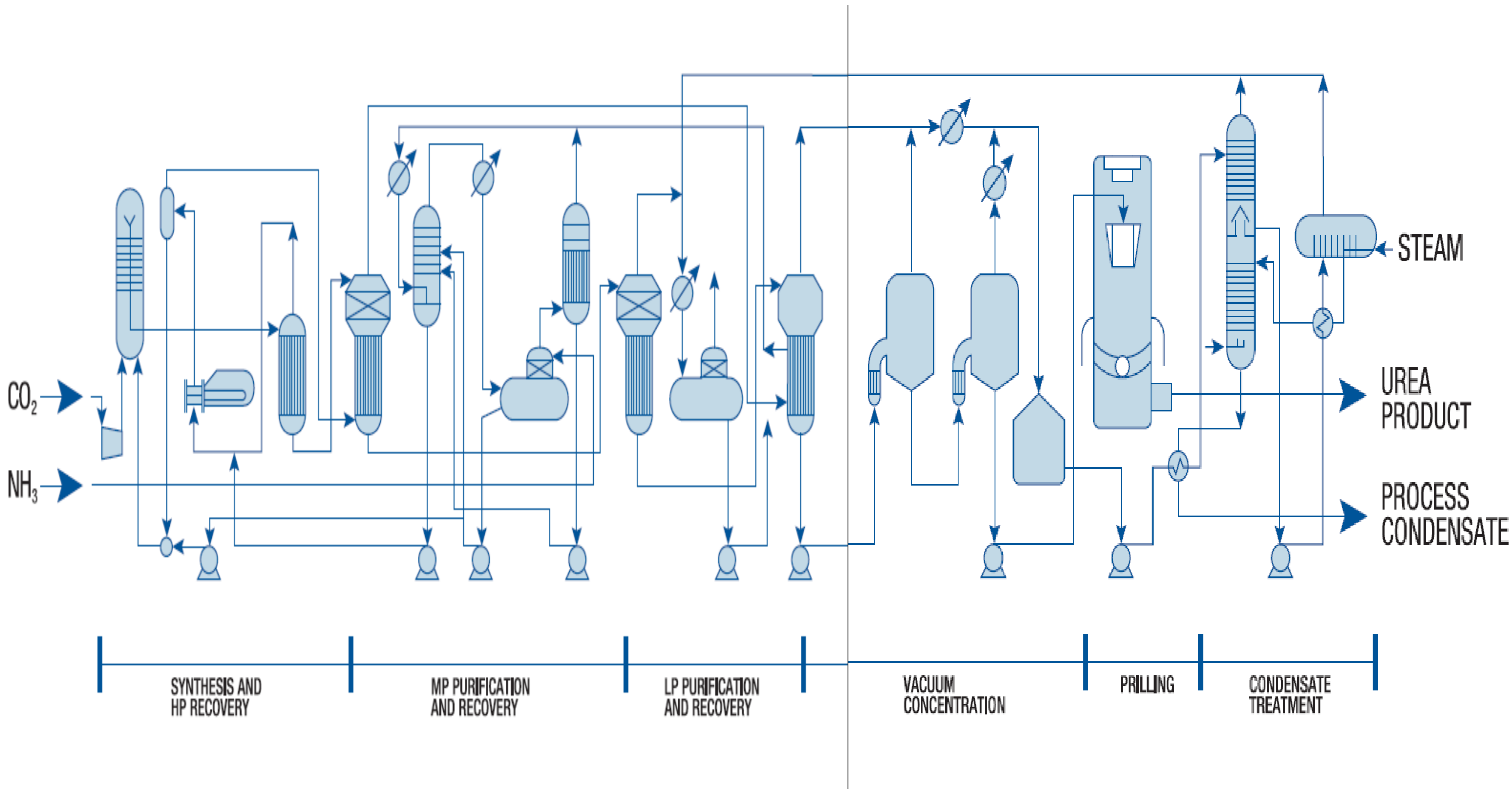



**Figure 9.4. Stamicarbon $CO_2$ Stripping Process.**

# Snamprogetti process

Six section

- Synthesis and high pressure (HP) recovery (160 bar)
- Medium pressure (MP) purification and recovery (17 bar)
- Low pressure (LP) purification and recovery (3.5 bar)
- Vacuum concentration (2 steps: 0.3 and 0.03 bar abs)
- Process condensate treatment
- Finishing: prilling and granulation




Snamprogetti Process Flow Diagram

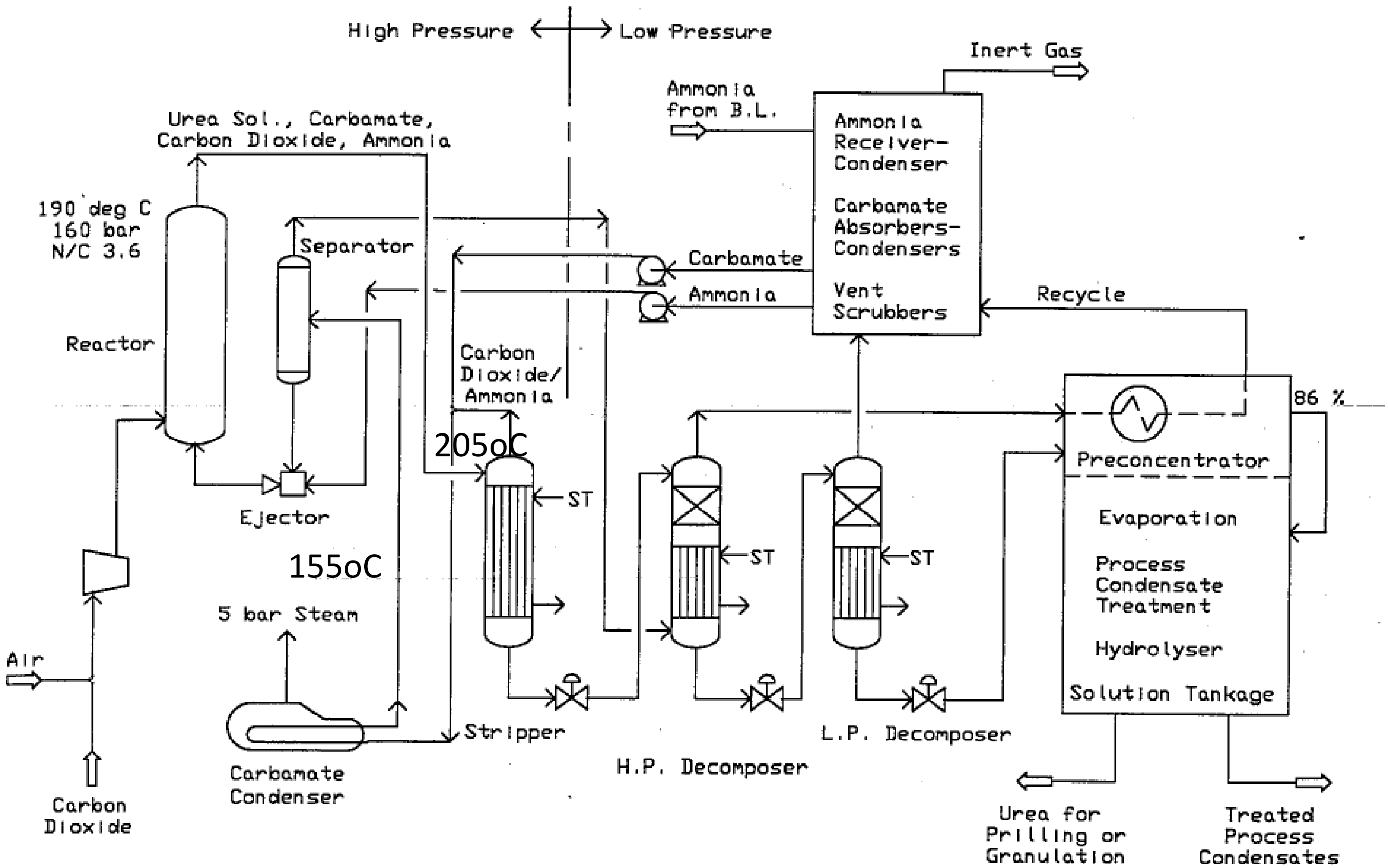
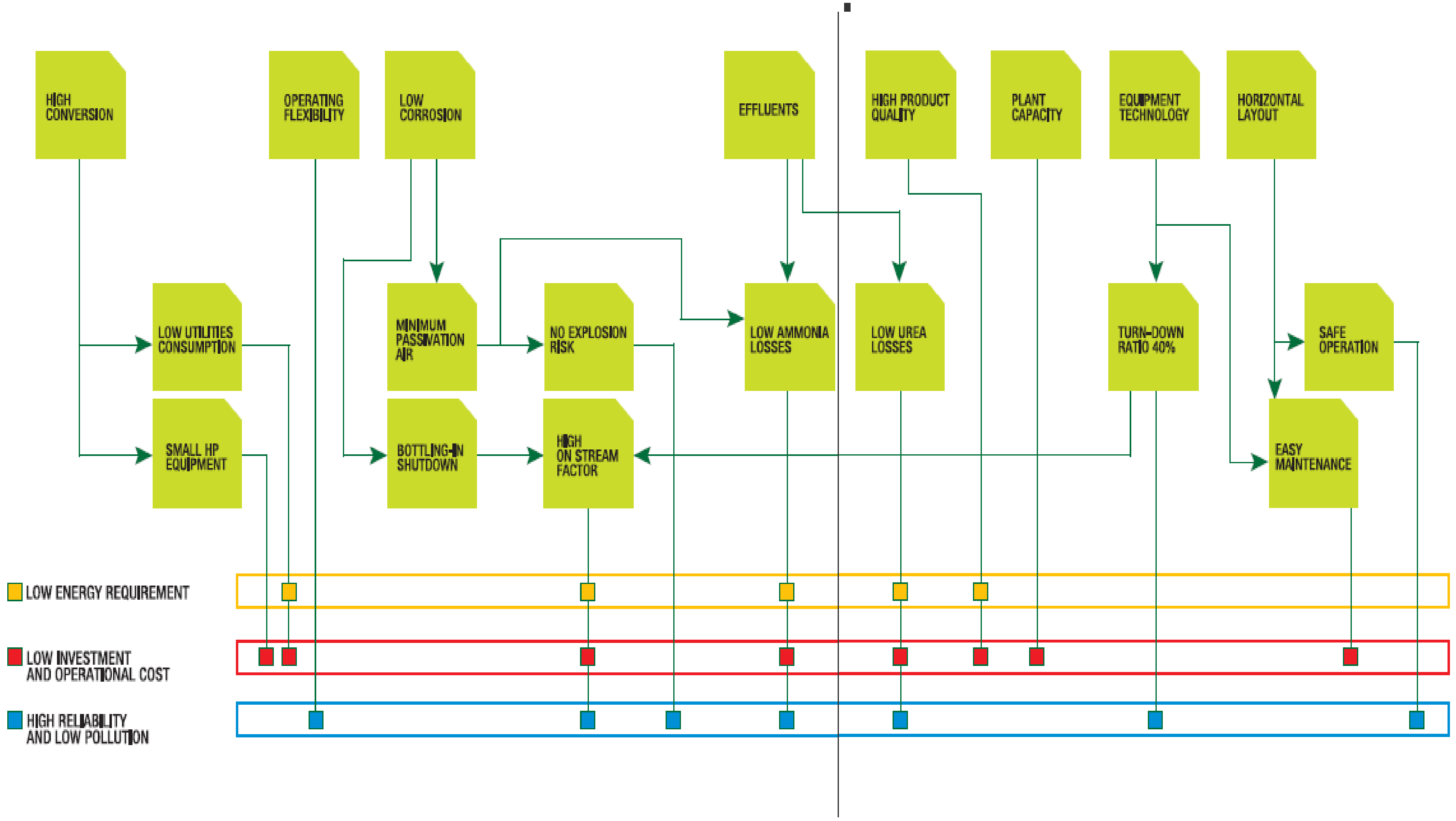



**Figure 9.5. Snamprogetti Thermal Stripping Urea Process.**

# Key Features of Snamprogetti Process



# ACES plant (UFFL)

1990 – Renovation. From 1994 – ACES is operating

Five section

- Synthesis sections
- Purification section
- Concentration and prilling section
- Recovery section
- Process condensate treatment section

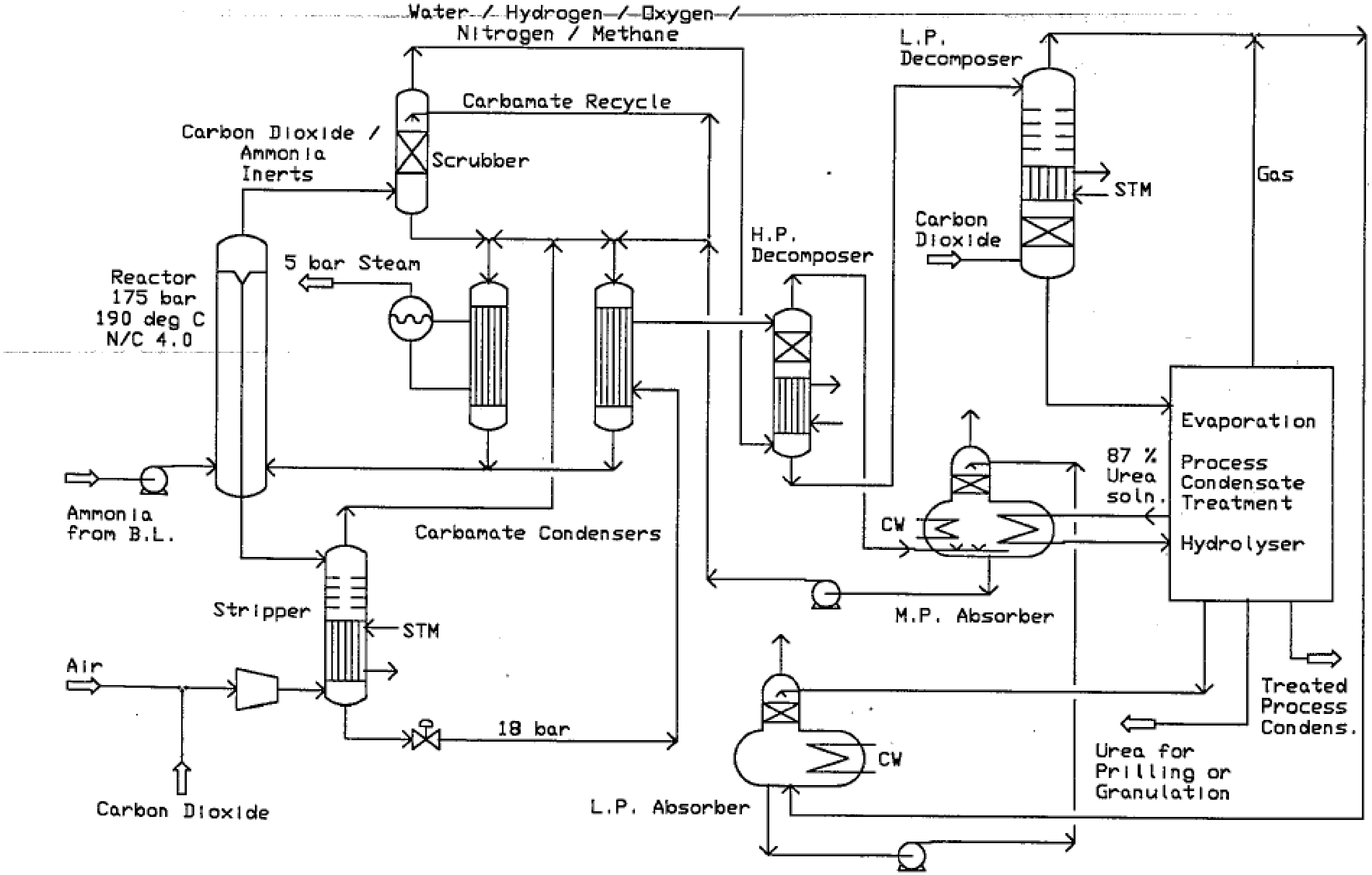



**Figure 9.6. TEC ACES Process.**

**Table 9.2. Urea Process Operating Conditions/Requirements [5]**

| | Snamprogetti Thermal Stripping | Stamicarbon $CO_2$ Stripping | TEC ACES Process |
|---|---|---|---|
| Reactor pressure, atm | 156 | 140 | 175 |
| Reactor temperature, °C | 188 | 183 | 190 |
| Molar $NH_3/CO_2$ ratio | 3.3-3.6 | 2.95 | 4.0 |
| Molar $H_2O/CO_2$ ratio | 0.5-0.6 | 0.39 | 0.6 |
| $CO_2$ conversion in reactor, % | 64 | 60 | 6.8 |
| $NH_3$ conversion in reactor, % | 41 | 36 | 34 |
| $CO_2$ conversion in synthesis, % | 84 | 79 | NA |
| $NH_3$ conversion in synthesis, % | 47 | 79 | NA |
| No. of high-pressure vessels – synthesis | 5 | 4 | 5 |
| Recirculation – stages | 2 | 1 | 2 |
| $NH_3$ consumption, t/t | 0.566[a] | 0.566[a] | 0.568 |
| $CO_2$ consumption, t/t | 0.735[a] | 0.733[a] | 0.735/0.740 |
| Import steam, t/t[b] | 0.950 | 0.920 | 0.80 |
| Cooling water, t/t[b] | 75 | 70 | 80 |
| Electricity, kWh/t[b] | 21-23 | 15 | 15 |
| Liquid effluent | | | |
| Free $NH_3$, ppmw | 2 | 1 | 5 |
| Urea, ppmw | 2 | 1 | 5 |
| Hydrolyzer steam pressure, bar | 38 | 25 | 25 |

Note: NA = not available.

a. Based on final product-urea granules containing ±4.5 kg formaldehyde/tonne product, using UF85 (urea+biuret 25%, formaldehyde 60%, water 15%).

b. Depending on plant location and available utilities, these figures can vary greatly. The plants can easily be designed for minimum steam or minimum electric power; the decision is on a cost basis.

# Class Test 2

Date: 14 August, 2010 (or Next available date after 14)

Syllabus: Stamicarbon, Snamprogetti and ACES process.

Free Tips: Memorize as much as you can !!!!