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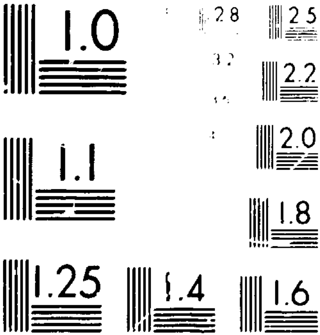
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COMBINED PRODUCTION OF AMMONIA AND UREA - A STUDY ON INTEGRATED UREA PROCESS WITH SHIFT GAS ~~SHIPPING*~~ STRIPPING.

by

Yu Bing Liang**

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ABSTRACT

One of the tendencies to develop the urea production is the combined manufacture of urea and ammonia, (simply known as Integrated Urea Process). This paper deals with the Integrated Urea Process with shift-gas stripping, which has been proved technically and economically feasible on a commercial unit.

The principle of stripping, results of laboratory experimentation and the selection of operating variables were described.

Finally, a techno-economic evaluation concerning the feasibility of this process was performed. The initial specifications of a 80 ton/day Integrated Urea plant using different feedstocks for ammonia production were presented.

I Introduction

For the conventional urea process the pure carbon dioxide from the decarbonation section in ammonia plant is pressurized and fed to the urea reactor. The use of shift gas containing approx. 18% CO_2 as stripping agent makes it possible to save the CO_2 compressor as well as to either eliminate (for natural-gas based ammonia plant) or simplify the decarbonation operation. In this case the shift gas is pressurized and directly supplied to thestripper where the carbon dioxide serves as starting material for urea production, while the remaining gas is recycled to the ammonia plant.

Based on this concept, we started experimentation since 1966 and successfully performed the pilot plant test. As a result, a commeraicl plant with an annual capacity of 10 thousand tons of urea was set up in 1974.

II. Principle of stripping with shift gas and laboratory experiments

During synthesis of urea the unconverted ammonium carbamate and the unreacted ammonia are always present in the urea solution. As it is obvious fron equation

$$2NH_3 + CO_2 \rightleftharpoons NH_4COONH_2 + Q$$

The ammonia carbamate decomposes into ammonia and carbon dioxide upon being heated. This decomposition process can be facilitated because of the reduced partial pressures of both NH_3 and CO_2 in gas phase when the shift gas containing about 18% CO_2 is passed through the carbamate containing urea solution. Hence, the stripping can take place at elevated pressures and lower temperatures. As the partial pressure of gaseous ammonia at the botton of stripper is nearly reduced to xero, the liquid phase ammonia concentration in equilibrium tends tends to approach zero accordingly. This desequilibrium leads to continuous decomposition of ammoniaum carbamate, and consequently the stripping purpose is achieved.

It was studied from the viewpoint of phase equilibrium whether the expected requirement aoulc be attained when the CO_2 in mixture with nitrogen was employed as stripping agent. The operating conditions and stripping efficiency were also studied under various pressures, with results shown in Figs. 1 and 2.

It concluded from these figures that (1) at a given pressure the yields of NH_3 and CO_2 distillation fractions fractions rose with increasing temperature; (2) at a given temperature the yields of NH_3 and CO_2 distillation fractions dropped with increasing pressure.

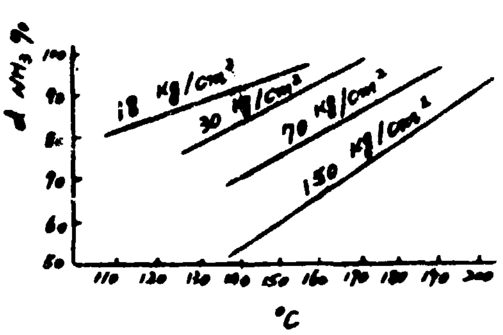


Fig 1. THE EFFECT OF TEMP. AND PRESSURE UPON THE YIELD OF NH_3 DISTILLATION FRACTION

Tab. 1. The residual content of NH_3 and CO_2 in urea solution with various,stripping stripping conditions

Ser. No.	Experimental variables				Composition of residue,% by weight		Stripping efficiency %	
	P,atm.g.	t, °C	,min	K,NM^3/kg liq.	NH_3	CO_2	NH_3	CO_2
1	30	145	40	3.3	0.26	0.63	99.8	98.7
2	30	155	40	1.7	1.36	1.85	99.1	95.0
3	45	145	60	5.0	0.38	0.99	99.7	99.8
4	45	165	60	5.0	0.38	0.67	98.8	98.9
5	70	145	40	3.3	2,41	3.10	98.2	90.2
6	70	165	40	3.3	1.51	2.13	99.1	94.8
7	150	177	60	9.6	1.44	2.38	98.9	97.8
8	150	185	60	2.6	5.74	6.01	96.9	88.1
9	200	175	60	9.6	2.02	3.19	99.2	95.2
10	200	185	40	6.4	3.93	4.51	98.6	94.2

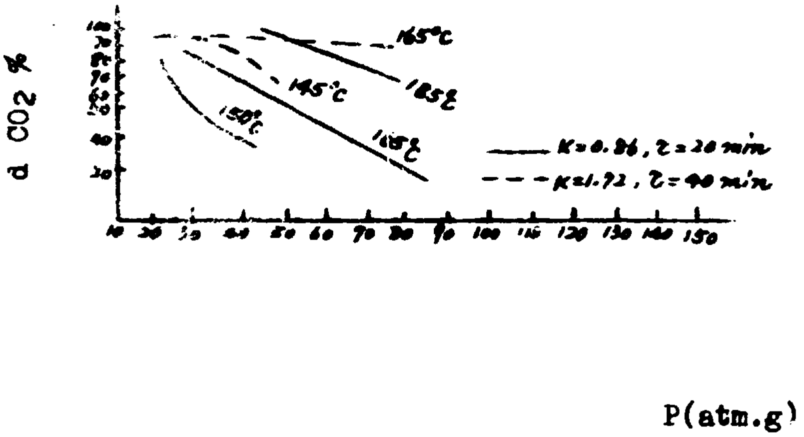


Fig 2. THE EFFECT OF TEMP. PRES. GAS TO LIQUID RATIO K AND RESIDENCE TIME UPON THE YIELD OF CO_2 DISTILLATION FRACTION

The experiment data listed in table 1, indicated that the desired residual concentrations of ammonia and carbon dioxide in urea solution could be reached under controlled conditions.

$$dNH_3 = \left(1 - \frac{NH_3 \text{ content in the stripped sol.}}{NH_3 \text{ content in the effluent from reactor}}\right) x\ 100\%$$

$$d_{CO_2} = \left(1 - \frac{CO_2\text{content in the stripped sol.}}{CO_2\text{cintent in the effluent from reactor}}\right) x\ 100\%$$

Table 1 implied that (1) the increased gas to liquid ratio K and residence time were in favour of distillation of NH_3 and CO_2 from urea solution; (2) at a given temperature the gas to liquid ratio K required to obtain the same final residual concs. of NH_3 and CO_2 in urea solution was practically proportional to the pressure.

The gas to liquid ratio K and the residence time were restricted by the acturl production conditions and engineering considerations. According to our laboratory experiments these two items could be deemed close to equilibrium due to the full contact between gas and liquid phases. Hence, it was necessary to work on the improvement of the heat and mass transfer in the stripper.

III. Brief description of the process

The flow sheet of Integrated Urea Process was presented in Fig 3, in which the gasification of heavy oil by apartial oxidation, conversion shift, purification and ammonia synthesis was omitted because of being identical to those of conventional processes.

Ammonia and ammonium carbamate feedstocks were delivered by pumps (20) and (210) to the urea reactor

(207). After being depressurized, the effluent from the reactor entered the top of stripping tower (208), where it was stripped counter currently with shift gas. The urea solution with a small amount of unconverted reactants was heated at reduced pressure and transferred to the flash vessel (219) for further decomposition and the recovery of ammonia and carbon dioxide. Finally this material was subjecfed to evaporation and granulation. The off gas from stripper entered the absorber (209) wher where the CO_2 was completely absorbed, with the resul tant ammoniumcarbsmste sent back to the urea reactor. The major portion of ammonia in the off gas was condensed in the condenser (211) and the remaining off gas passed to the ammonia recovery tower (213), where the ammonia was washed and recovered in the condensate from the flash unit and evaporation unit. The concentrated aqueous ammonia thus obtained served as absorbong agent for the CO_2 absorber, while the hydrogen and nitrogen mixture was recycled to the ammonia synthesis loop.

IV. Selection of operating variables and discussion

(i) Urea reactor

Our experiments on gas-liquid equilibrium of NH_3-CO_2-H_2O Urea system under high temperatures and pressures indicated that the conversion of CO_2 at equilibrium could be calculated by the following equations:

$$Xeq = 14.8/L - 1.322L^2 + 20.70\,WL - 1.830WL^2 + 167.6W - 1.217WT + 5.908t - 0.01375t^2 - 591.1$$

Where Xeq -- conversion of CO_2 at equilibrium, %

L - molar ratio of NH_3/CO_2 in the original liquid
W - phase ratio of H_2O/CO_2 in the original liquid phase
t - operating temperature, °C.

It is concluede from the measurements made on the pilot plant and commercial unit that the above-mentioned semiempirical equations could serve as the basis for design and production control.

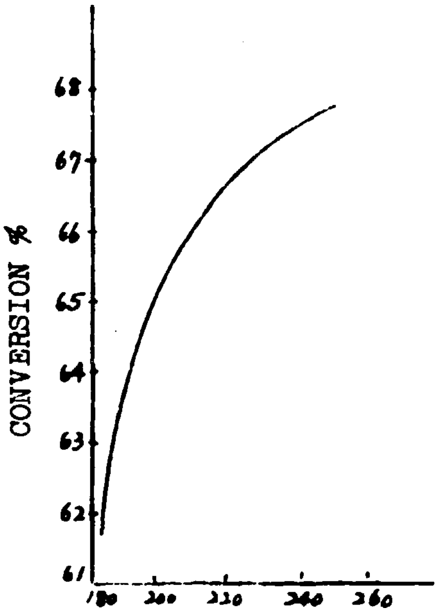
To obtain the optimum operatiing pressure, it was necessary to determine the equilibrium pressure of the system through the following equations

$$P_{eq} = 54.75L - 10.10\,WL - 90.25\,W - 0.1502\,Lt + 2.059 \times 10^4 \frac{W}{t} - 3.581t + 2.099 \times 10^{-2} t^2$$

where Peq — the equilibrium pressure (atm. gauge), with other symbols identical to heretoabove.

As a rule, a giver amount of air was introduced into the system to prevent the urea reactor from corro corrosion. The presence of inerts tended to increase the equilibrium rpressure. The operating pressure should be much higher than the equilibrium value to facilitate the formation of carbamate from ammonia and carbon dioxide. Fig. 4 demonstrated the operating pre pressures as function of CO_2 conversions obsered from the pilot plant test. Obviously, the increase in CO_2 conversion became slower when the pressure exceeded 220 atm. (gauge). Therefore, taking investment and energy consumption etc into consideration, the operating pressure not higher than 220 atm. (gauge) was preferred.

1. Feedstock : $NH_3.CO_2$ - 4.6 (mol ratio)
   H_2O/CO_2 - 0.7(mol ratio)
2. Reaction temp: 184- 188^{o}C



Reaction pressure (atm. g)

Fig. 4. Conversion versus operating pressure in reactor

(2) Stripper

The stripping pressure (including pressures in the absorber and the ammonia recovery column) should be selected from consideration of entire process.

Operation at low pressure, though favourable to the stripping process, results in an increased amounts of wash water in the ammonia recovery column. However, experiments showed that it was difficult to reduce the molar ratio of H_2O/CO_2 in reactor below 0.9, even at a pressure as high as 45 atm. (gauge). This characteristic was certainly unfavourable to the increase in conversion of CO_2 in reactor.

By increasing pressure not only could the temperature of effluent from absorber be raised but also a better recovery of heat from the absorber be realized. However a high pressure must be accompanied by a corresponding higher temperature in stripper so that the required stripping efficiency is assured, enabling the molar ratioa of H_2O/CO_2 at reactor inlet to be kept below 1.0. With increasing stripping temperature the requirement for construction material of stripper becomes more critical. The pressure set for experiments was in the range of 45 - 150 atm. (G).

The stripping efficiency was greatly affected by the structure of stripper. Experiments showed that after adiabatic expansion the urea solution passed through the rectification section of stripper, and the water vapor as the high-boiling component condensed off and consequently a less amount of water was entrained into the downstream absorber, which was naturally beneficial to the balance of water for the entire system.

The lower section of stripper was provided with a perforated plate which contributed to the uniform distribution of gas and to the adiabatic stripping action so that the liquid effluent temperature was reduced from 140°C to below 130°C and a further decrease in NH_3/CO_2 ratio observed.

With respect to the film type strippingtower, the extent of evenness of loquid destributution and then stability of liquid film not only affect the stripping efficiency and the throughput of tower, but also might cause corrosion to the equipment at elevated temperatures.

It can be seen from the resultw listed in table2, that the steam pressure, hence the stripping temperature rose with increasing stripping pressure, althrough the yieods of ammonia and ammonium carbamate were still kept reasonable.

The biuret content was determined at relatively high stripping temperatures when the operating pressures were over 120 atm. (G). The relevant figures were tabulated in Tab. 3. Although the stripping efficiency was improved, when the steam pressure in the lower heater was enhanced to approx. 19.5 atm. (G), an appreciable amount of biuret formed, which is of course undersirable in commercial production.

Table. 2. Operating data of stripper at different pressures

Ser.	Temp. °C				Pressure, atm. (G)			Efficiency %	
No.	Urea sol. after depressurization	Inlet of heater	Outlet of heater	Bottom of tower	Inside tower	Steam for the upper heater	Steam for the lower heater	d_{NH_3}	d_{CO_2}
1.	139	155	146	124	45	6.5	7.9	97.2	90.2
2.	146	161	138	127	60	6.9	8.3	94.7	83.9
3.	173	162	93	83	120	20.4	10.7	96.6	78.6
4.	183	171	80	99	150	20.0	10.0	96.0	79.1

Table. 3. The changes in biuret content during stripping

Concentration of biuret in urea sol. (dry basis) %				Steam pressure for stripping, atm. (G)		Concentration in effluent from stripping % by wt.	
Exit of reactor	Inlet of upper heater in stripper	Inlet of lower heater in stripper	Effluent from the bottom of stripper	Upper heater	Lower heater	NH_3	CO_2
0.33	0.33	0.48	0.56	20.0	9.0-12.0	1.19	3.09
	0.30	0.45-0.60	1.72	20.0	19.5	0.52	1.67

(3) Carbon dioxide absorber

To determine the operating parameters of absorber the ammonium carbamate phase region in NH_3-CO_2-H_2O system was studied. The equilibrium vapor pressures of this system at 120°C were presented in Fig. 5. It has been proved in practice that these phase equilibrium data of tertiary system could be employed to guide the absorption operation at relatively low pressures.(1)

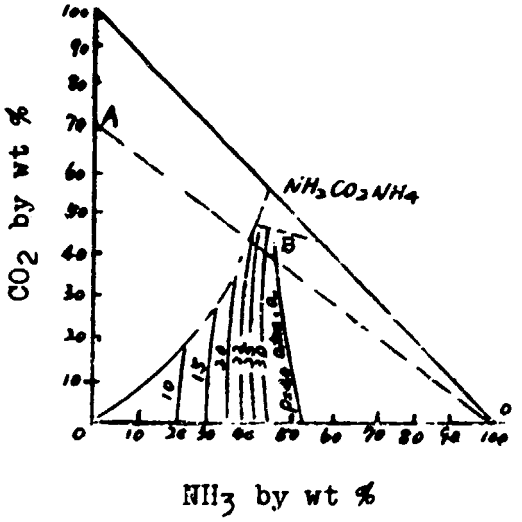


Fig. 5. The equilibrium vapour pressure of NH_3-CO_2-H_2O system AT 120 °C

(4) Condensation and recovery of ammonia from the nitrogen and hydrogen mixture.

Results of measurement showed that the Larson formula after being corrected was adaptable for the calculation of ammonia concentration in the gaseous mixture of nitrogen, hydrogen and ammonia during condensation under high pressure (2,3).

In case of water cooling the tail gas from condenser inevitably contains a given amount of ammonia which should be trapped by washing to minimize its loss and to satisfy the requirements of the downstream CO purification unit. Therefore, the gas-liquid equilibrium data of NH_3-H_2O system were measured. We studied the relationship of the gas-liquid equilibrium of the NH_3-H_2O- H_2-N_2 quaternary system. The gas phase non-idealness was described by use of the modified Redlich-kwong equation of state whereas the liquid phase non-idealness by use of the empirical model of activity coefficient for ammonia - water system.

(5) The thermal balance in urea reactor [illegible] approaches to minimizing the steam consumption.

For conventional process the autothermic balance in reactor is established by adjustment of the NH_3 feesstock and operating temperature. In the present process the carbon dioxide in the form of shift gas is transfered to the stripper instead of feeding the pure carbon dioxide directly to the reactor. As the ammonium carbamato formation which is a strongly exothermic recation took place in the absorber, the heat rewuired for maintaining the reactor temperature and for dehydration of ammonium carbamate urea must be furnished from some other external source. Experiments showed that the reactor temperature could reach 188°C, when the ammonia and carbamate were heated seperately only to 180°C. This difference in temperatures implied that the dissolution heat of supercritical ammonia in urea solution would be larger than that required for the conversion of carbamate into urea. The heat value data could be used in heat balance calculation.

The preheating of ammonia and carbamate to maintain the thermal balance in reactor was primarily restricted by the operating temperatures of construction materials. The successful adoption of titanium stripper in the pilot plant makes it possible to operate this stripper and the reactor isobaricly. In this manner, the reactor temperature could be maintained by recycling in gas phase the NH_3 and CO_2 which in turn were obtained by heating the effluent from the reactor. The steam consumption, as a result, would be decreased accordingly.

(6) Materials and corrosion prevention

The main equipments in this plant were manufactured of double-phase stainless steel Cr17Mn14Mo2N having high mechcnical strength, corrosion resistance and better adaptability toward low oxygen content as compared with austenitic stainless steel Cr18Ni12Mo2. As it has been demonstrated by experiments, the minimum critical oxygen amount rewuired for passivation of the former and its "passivation current density (the height of activation peak) were lower in comparison with those for the latter. In order to increase the stripping temperature, titanium column was used in the pilot plant. Through experimentation it has been revealed that due to its higher allowable operating temperature, corrosion resistance and better suitability to low oxygen content than those of Cr17Mn14Mo2N, this material was especialy favourable for increasing stripping pressure and using the "thermal decomposer" to heat the effluent from urea reactor.

V. Commercialization and techno-economic evaluation

(1) Commercial production

The CO_2 concentration in shift gas varies with different feedstocks (liquid or gaseous hydrocarbons and coals) and gasification methods. An excess of carbon dioxide is always available in urea production unless the gaseous hydrocarbons are involved. Consequently it is necessaary to install a partial decarbonation unit so as to balance the ammonia for the whole system.

A finite amount of air introduced into the system to protect the equipments for urea production from corrosion finally reaches the CO purification unit after passing through the sections of urea synthesis, stripping, absorption and ammonia recovery. In practice the normal operation of carbon monoxide purification unit is affected by no means should suitable measures be taken.

(2) The techno-economic comparison between " medium Pressure Integrated Process " and " Total Recycle Process " for urea production

The techno-economic data of a 220 ton/day ammonia plant (or equivalent to a 350 ton/day urea plant) with different feedstocks were compared between "Medium Pressure Integrated Process " and " Total Recycle Process " and summerised in table 4. It is evident that due to its simplified technology, the Medium Pressure

Integrated Urea Process is characterized by the energy con consumption of 1.22 - 1.46 x 10^6 KCal/ton ammonia, so the production cost of urea can be reduced. In case of using natural gas as feedstock then investment and production cost are even more less and reduced by 7.9 and 6.2% respectively because no decarbonation section is needed.

(3) Techno-economic data of a 50 ton/day NH_3 (or 80 ton/day urea) plant based on Integrated Process

Table 5 listed relevant specifications of a 80 Ton/day urea plant using anthracite, fuel oil and natural gas as feedstocks.

Conclusions

(1) The feasibility of the Medium Pressure Integrated Urea Process has been verified by pilot plant tests and trial production. The control and measurement mothods for combined production were established, and the design and production data obtained.

(2) In the Integrated Urea Process the CO_2 compressor is eliminated by feeding CO_2 into the urea reactor in the form of ammonium carbamate. Meanwhile, the purification stopin the ammonia production can be simplified as a result of simultaneous decarbonation. Another feature of this process is that the load of " copper solution wash or " methanation " is greatly alleviated because of the extremely low concentration of CO_2 (a few fractions of ten thousandth.) in the off gas from urea system.

(3) By stripping with shift gas and by flash distilling the effluent from stripper, the ammonia and CO_2 can

almost entirely be driven off from the urea solution, which enables the equipments for low pressure decomposition and recovery to be eliminated and urea production process simplified.

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Table. 4. A comparison between different routes of urea production.
(220 ton/day NH_3, 350 ton/day Urea plant)

Ser. No.	Item	Feedstocks					
		Lump coal		Oil		Natural gas	
		CSTRP	MPIP	CSTRP	MPIP	CSTRP	MPIP
1	Investment for NH_3 and urea plants,%.	100	96.7	100	96.0	100	92.1
2	Production cost per ton of NH_3, %.	100	94.1	100	93.6	100	88.9
3	Production cost per ton of urea, %	100	96.9	100	96.6	100	93.8
4	Energy consumption x 10^6 KCal/ton	15.99	14.53	13.73	12.32	9.98	8.76
	%	100	90.9	100	89.7	100	87.8
5	Energy consumption x10^6 KCal/ton urea	11.19	10.88	9.87	9.58	7.67	7.47
	%	100	97.2	100	97.0	100	97.4

MPIR - Medium Pressure Integrated Process.

CSTRP - Carbamate Solution Total Recycle Process

Tab. 5. Specification of a 50 ton/day ammonia (80 ton/day urea) plant based on Integrated Process.

Ser. No.	Item	Feedstocks		
		anthracite	fuel oil	natural gas
1	Investment of NH_3 and urea plants, %	100	117.26	94.98
2	Workshop production cost of NH_3, %	100	96.47	80.59
3	Energy consumption, KCal/ton NH_3	17.44×10^6	14.81×10^6	11.09×10^6
4	Ammonia consumption, Kg/ton urea	590	590	590
5	Workshop production cost of urea, %	100	97.51	86.28
6	Energy consumption, KCal/ton urea	12.6×10^6	11.04×10^6	8.85×10^6
7	Feedstock and energy consumption within battery limits			
	(1) Feedstock	67.0ton/day	41.8 ton/day	52540 NM^3/day
	(ii) Calorific value	7000KCal/day	9740 Kcal/day	8550 KCal/day
	(iii) Electricity, Kw Hr	3500	2980	2340
	(iv) Cooling water at 32°C, M^3/hr	1930	1530	1330
	(v) Steam at atm., ton/hr.	17.6	11.4	6.1
	(vi) Deaerated soft water, M^3/hr	6.3	6.3	7.6
	(Vii) 99.8% Oxygen, NM^3/hr	-	1390	-
	(Viii) 99.99% Nitrogen, NM^3/hr	-	1540	-

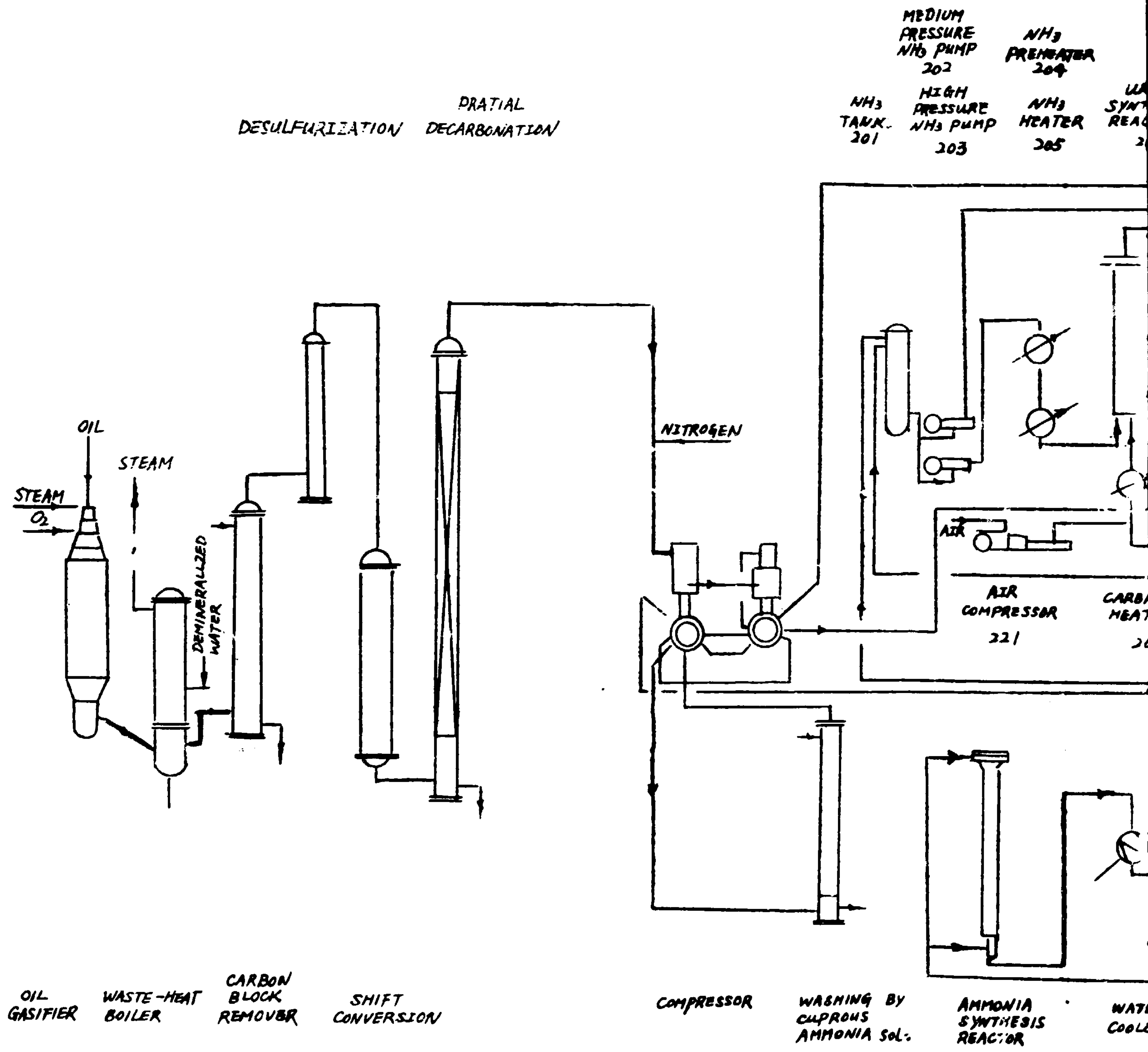
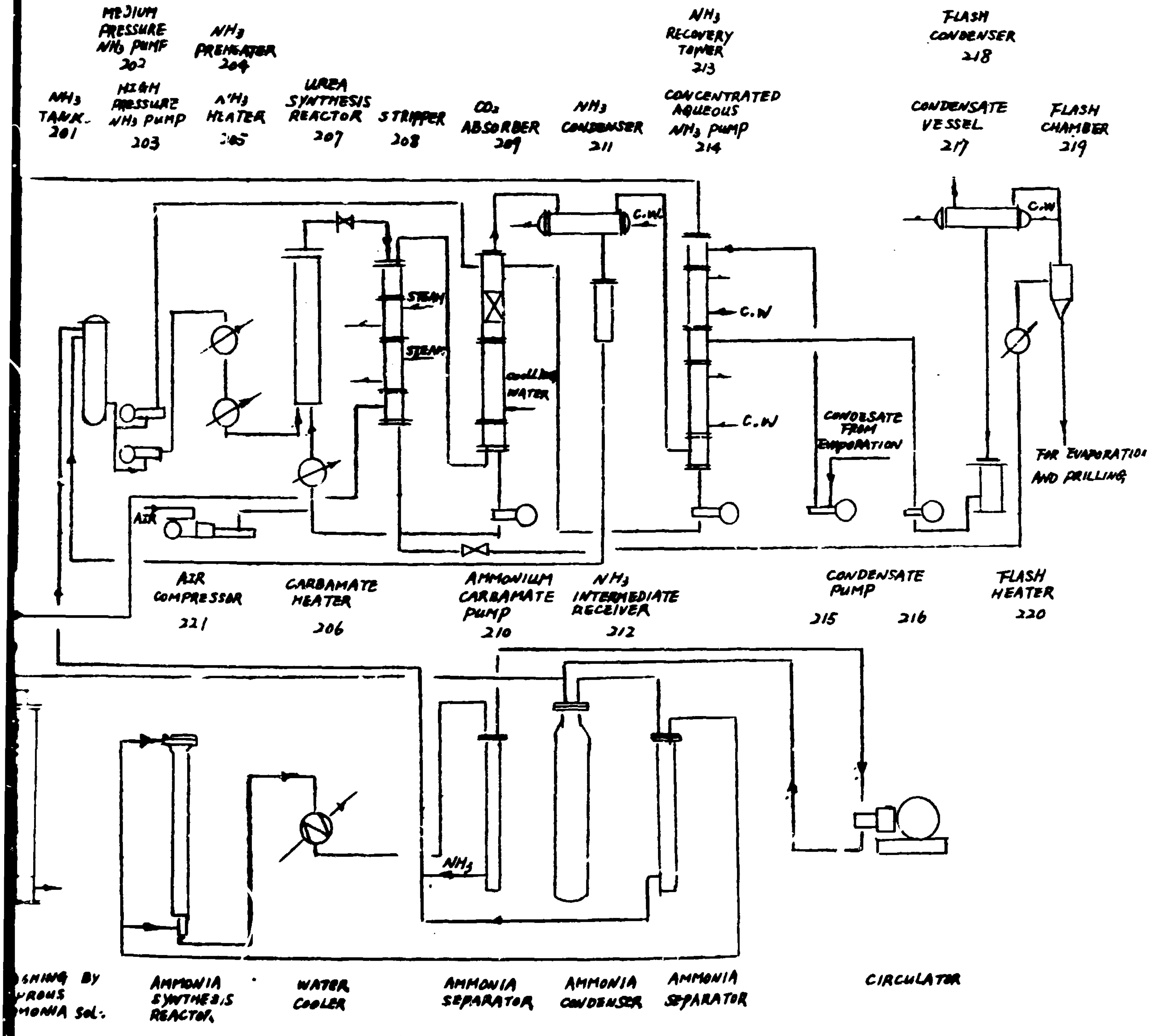


FIG. 3 SCHEME OF MEDIUM PRESSU

SECTION 1



5 SCHEME OF MEDIUM PRESSURE INTEGRATED UREA PROCESS

SECTION 2