

A Direct Synthetic Urea Process¹

H. J. Krase,² V. L. Gaddy, and K. G. Clark

FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS, WASHINGTON, D. C.

THE following process for the synthesis of urea from ammonia and carbon dioxide was developed because of the rapidly increasing interest in concentrated fertilizers and the realization that urea would undoubtedly be one of the more important concentrated nitrogen carriers of the future. Urea is also of interest in the rapidly growing field of organic plastics (1). Whereas urea synthesis from calcium cyanamide is a relatively old idea, as chemical developments now go, the industrial synthesis of this important chemical directly from ammonia and carbon dioxide is comparatively recent, and has not received the attention it deserved, in this country at least.

The importance with which this material has been viewed in Germany is illustrated by the number of patents (2, 3, 4, 5, 7, 11) granted in this country covering the German developments. A German process is said to be operating according to the method described in one of these patents (3).

Flow Diagram

A representative flow sheet of the process, as developed at this laboratory, is illustrated in Figure 1. The starting materials are liquid ammonia and gaseous carbon dioxide, the former being obtained directly from the synthetic ammonia plant and the latter by the process described by Krase and Hetherington (15) or by other suitable means. The quantities handled by the various pieces of equipment are based upon a net throughput of 10 tons of ammonia per day, and upon an assumed conversion of 40 per cent in the urea autoclave.

The flow sequence of the process is briefly as follows: The liquid ammonia from the synthesis plant enters a liquid pump of the hydraulic type, which acts also as a measuring device. The carbon dioxide, after liquefaction, enters a similar pump which may be actuated by the same power source. If this is the case, adjustment of the flows is effected by changing the stroke of the pump so that the liquids are delivered in the molecular ratio $2\text{NH}_3:\text{CO}_2$. Both liquids then enter the urea autoclave, where reaction and conversion to urea take place. After leaving the autoclave the charge, now consisting of a liquid mixture of urea, water, and carbon dioxide compounds of the ammonia, enters a still in which the dissociation of the ammonium compounds is accomplished by means of heat. The urea leaves the still in aqueous solu-

A continuous process for the synthesis of urea from liquid ammonia and liquid carbon dioxide has been developed and described. A small unit for the production of 175 pounds of urea per day has been designed, constructed, and successfully operated. An exothermic autoclave reaction is indicated both by calculation and observation. Thirty-five to thirty-seven per cent conversions of the reactants to urea have been attained at an applied temperature of 153° C. in a reaction period of less than 2 hours.

tion. The ammonia and carbon dioxide leave the still as gases to enter a regenerator in which the ammonia is absorbed in an aqueous solution. The carbon dioxide discharges from the regenerator into the compression system. The working of the regenerator is described by Krase and

Hetherington (15), and is based on the work of Clark and Krase (10) on the partial pressures of carbon dioxide and ammonia in the ammonium carbonate-ammonium nitrate system. The ammoniacal liquor from the regenerator enters the ammonia still from which the ammonia is obtained as a gas and returned to the compression system for liquefaction and re-introduction into the autoclave. New features only are shown in the flow sheet. Coolers for liquefying the compressed ammonia and carbon dioxide, as well as driers for these gases, are required.

Pumping Liquid Ammonia and Carbon Dioxide

The pump used in the experimental plant for introducing the liquid ammonia and carbon dioxide into the urea autoclave is a single-acting hydraulic type. (Figure 2) The two pistons are actuated by means of a single crankshaft driven through a train of gears by means of a 0.5-horsepower induction motor. The shaft turns at about 100 r. p. m.

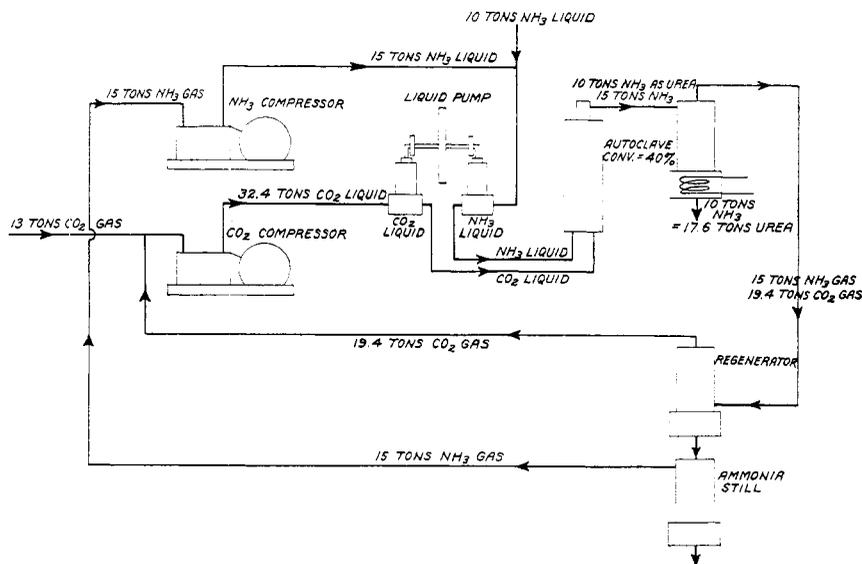


Figure 1—Flow Diagram for a Direct Synthetic Urea Process

The stroke-changing mechanism is shown at the left of the pump. By this means the stroke may be varied from 0 to 1.6 inches. A 3-inch steel scale graduated in hundredths of an inch and screwed on the crank plate allows an accurate setting of the stroke to be made.

To pump liquid ammonia and carbon dioxide, where these liquids are supplied from cylinders at room temperature, it is necessary to cool the liquids and the cylinder blocks below room temperature in order to prevent vaporization of the

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² Present address, Federal Phosphorus Co., Anniston, Ala.

liquid during the suction stroke of the pump. The net minimum feed pressure required to cause a sufficiently rapid flow of liquid through the valve ports completely to fill the cylinder of the pump at each stroke can be estimated roughly as that necessary to force open the inlet valve against the combined resistance offered by the spring tension plus the vapor pressure of the liquid at the temperature of pumping. Practically, a pressure appreciably higher than this was used. It is also possible to provide adequate feed pressure for the

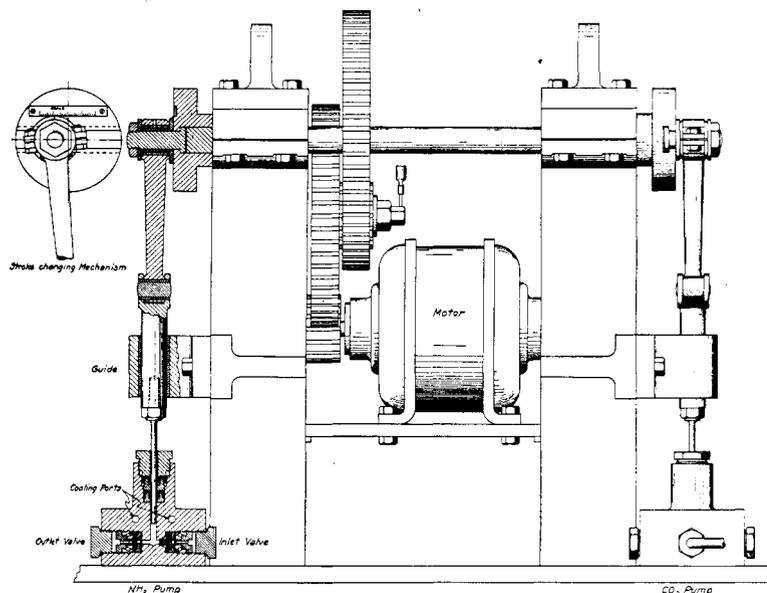


Figure 2—Liquid Ammonia and Carbon Dioxide Pumps

pump by raising the temperature of the liquid ammonia and carbon dioxide storage vessels above that of the pump. In this case artificial refrigeration would not be required. However, in the case of carbon dioxide the proximity of the critical temperature (31.1° C.) to room temperature (about 20° C.) makes for a rather narrow working temperature range. In the experimental plant it was found more convenient to cool the pump cylinders and the liquids by circulating ice water. It was found in the case of carbon dioxide before refrigeration was employed that even the small amounts of heat generated by friction between piston and packing caused appreciable variations in the amount of liquid carbon dioxide delivered, apparently because of the large fluctuations of the specific volume of liquid carbon dioxide with temperature in the vicinity of the critical point.

The densities of liquid ammonia (δ) and carbon dioxide (β) at various temperatures are given in Figures 3 and 4. Unfortunately the density of liquid ammonia at pressures higher than the saturation pressure is unknown; the change in density at higher pressures is probably small compared with that of carbon dioxide. The compressibility of liquid carbon dioxide is well known, so that this factor can be taken into account in the pump design.

The weights of liquid delivered by the pump for various stroke adjustments are shown in Figure 5. These values were obtained by pumping at constant pressure into a tared steel cylinder for a measured period of time, and then weighing the cylinder and liquid. The back pressure was in all cases 1500 pounds; the inlet pressures of ammonia and carbon dioxide were the normal vapor pressures of these liquids in their storage cylinders at the room temperature.

The slip of the pump can be estimated by calculating the piston displacement and the volumes of the respective liquids, as follows:

| | |
|--|--------------------|
| Stroke..... | 1 inch (2.54 cm.) |
| Piston displacement..... | 129.5 cc. per min. |
| Weight CO ₂ delivered at 1500 lbs. (100 atm.).. | 107 grams per min. |
| Volume CO ₂ delivered..... | 110.5 cc. per min. |
| Slip (corrected for compressibility)..... | 14.5 per cent |
| Weight NH ₃ delivered at 1500 lbs. (100 atm.).. | 78 grams per min. |
| Volume NH ₃ delivered..... | 121.8 cc. per min. |
| Slip and compressibility..... | 6 per cent |

Urea Autoclave

The urea autoclave (Figure 6), originally a small naval gun, was prepared for our purpose by the Washington Navy Yard.

The steel shell was 4.5 inches internal diameter and 7 feet long, with 1.25-inch wall at the thinnest part. The interior was lined with a 0.5-inch lead liner cast in place. Blow holes in the liner were closed by rolling with an internal expanding roller.

The steel heads were held in place by means of nickel-steel studs and bolts. It had originally been planned to machine the heads from special high nickel-chromium alloy castings. However, because of the difficulty in obtaining two sound castings of this material, this plan was abandoned; a nickel-chromium alloy head was used for the base and an ordinary carbon steel head for the top of the autoclave. The carbon steel head, however, was badly corroded after approximately 3 months' experimentation. The lower head contained the two inlet valves, one for ammonia and one for carbon dioxide. By using long stem valves with the seats within the autoclave proper, all danger of freezing up the inlets with ammonium carbamate was eliminated. The top head carried the outlet-valve and pressure-gage connections. It was found desirable to provide a small steam port within this head to prevent freezing of the discharge ports by the drop in temperature caused by the rapidly expanding gases passing through the outlet.

A steam jacket was welded on the side of the autoclave as shown and was connected to both the steam and the cold-water supply. This made it possible rapidly to melt or freeze the charge within, according to the exigencies of experimentation.

Connection to the pressure gage was made through an outlet on the top head as shown in the drawing. The connection between the gage and the head embodied a mercury trap, kept hot by means of an electric heating coil to prevent solidification of the autoclave products. The Bourdon tube of the gage was filled with oil.

The volume of the autoclave was 15.45 liters. The density of the charge at 150° C. was determined by C. F. Weston, formerly of this laboratory, to be 1.29. It therefore required 19.9 kg. of the charge to fill it. Pumping at the rate of 250 pounds (113.4 kg.) of ammonia per 24 hours (139 mols of carbamate per hour) with a conversion of 40 per cent, the plant should produce 175 pounds (79.4 kg.) of urea per day. At this rate the volume of the autoclave allows for

$$\frac{19.9 \times 250 \times 78 \times 454}{24 \times 34 \times 1000}$$

or 1.83 hours for the reaction to proceed to a 40 per cent conversion.

Thermal Considerations

Complete data are not available for the accurate calculation of the thermal effects encountered in the autoclave reactions. However, it seems worth while, with certain approximations, to estimate the probable order of magnitude and sign of this effect.

For convenience in calculation the ammonia and carbon dioxide are assumed to vaporize and to react forming solid

carbamate at 25° C., which is then heated to fusion at 145° C., and the liquid heated to 150° C., the conversion to urea taking place at the latter temperature.

HEAT OF VAPORIZATION OF AMMONIA AND CARBON DIOXIDE—The liquid ammonia and carbon dioxide entering the autoclave at approximately 4.5° C. (40° F.) are vaporized and heated to 25° C. (77° F.). The heat absorbed by this process is then

| | | |
|---|-------------------------|-----|
| | <i>B. t. u. per lb.</i> | |
| Heat in liquid NH ₃ at 40° F. | 86.8 | (8) |
| Heat in vapor NH ₃ at 77° F. | 630.2 | |
| Heat change | 543.4 | |

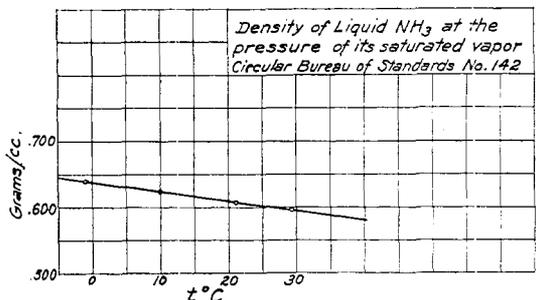


Figure 3—Density of Liquid Ammonia

One hundred and thirty-nine mols of carbamate per hour are equivalent to 10.4 pounds of ammonia per hour. Therefore, the hourly heat requirement for vaporization of the ammonia is 10.4 times 543.4 B. t. u., or 5650 B. t. u. per hour.

A similar calculation for the carbon dioxide which amounts to 13.5 pounds per hour gives

| | | |
|---|-------------------------|------|
| | <i>B. t. u. per lb.</i> | |
| Heat in liquid CO ₂ at 40° F. | 4.7 | (16) |
| Heat in vapor CO ₂ at 77° F. | 83.2 | |
| Heat change | 78.5 | |

The hourly heat requirement = 13.5 × 78.5 = 1060 B. t. u. per hour

HEAT OF FORMATION AND SPECIFIC HEAT OF CARBAMATE—The heat of formation of ammonium carbamate from gaseous ammonia and carbon dioxide was found to be 38,060 calories per mol at constant pressure (9). For 139 mols this amounts to 21,000 B. t. u. per hour at, say, 77° F.

Assuming that ammonium carbamate is formed at 25° C. (77° F.) it is necessary to heat it to its melting point which is 145° C. (293° F.), as determined by L. A. Pink of this laboratory, and then to heat the molten liquid to the autoclave tem-

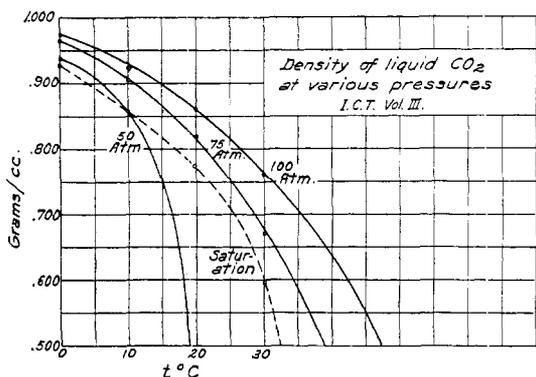


Figure 4—Density of Liquid Carbon Dioxide

perature, 150° C. (302° F.) Because of the uncertainty in the specific heat of carbamate, the average heat of the solid and molten carbamate has been taken, calculated by Kopp's law, to be 36.4 calories per mol per degree (9). The hourly heat

requirement because of the heat capacity of the carbamate is then

$$36.4 \times (150 - 25) \times 139 \text{ mols} = 632,450 \text{ calories per hour, or } 2510 \text{ B. t. u. per hour}$$

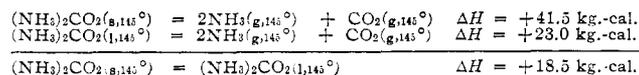
HEAT OF FUSION OF AMMONIUM CARBAMATE—The heat of fusion of ammonium carbamate, in the absence of experimental data, was estimated from the vapor-pressure curve of Briner (6). The plot of the vapor pressure against the temperature in the usual form (Figure 7) results in two straight lines intersecting at the melting point, and allowing the heat of sublimation of the solid and the heat of vaporization of the molten carbamate to be calculated with the aid either of the van't Hoff

$$\frac{d \ln K}{dT} = \frac{\Delta U}{RT^2}$$

or the Clausius-Clapeyron

$$\frac{d \ln P}{dT} = \frac{\Delta H}{T\Delta V}$$

equations. However, in using these equations, it is necessary to take into account the fact that carbamate is completely dissociated (12) into ammonia and carbon dioxide in the gas phase; otherwise one-third the true value will be obtained. The difference between the heat of sublimation and the heat of vaporization is the heat of fusion of the carbamate. The reactions involved may be written:



The heat of fusion is then 18.5 kilogram-calories per mol (78 grams) or 237 calories per gram.

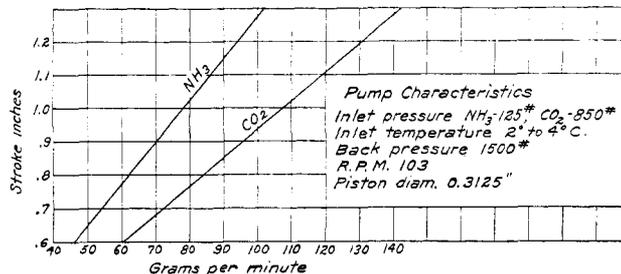
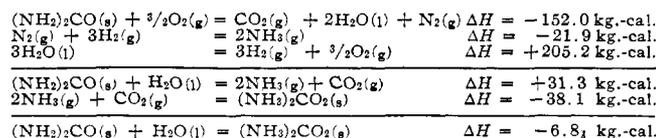


Figure 5—Characteristics of Ammonia and Carbon Dioxide Pumps

The above value gives for the hourly requirement of the heat of fusion

$$\frac{139 \times 18.5 \times 1000}{252} = 10,200 \text{ B. t. u.}$$

HEAT OF REACTION: (NH₃)₂CO₂ = (NH₂)₂CO + H₂O—Although the heat of this reaction at 25° C. can readily be estimated from ordinary thermochemical data (14), it is necessary in estimating the heat of reaction at 150° C. to have a knowledge of the change in heat content of the substances involved between these two temperatures. The unknown factors may be estimated then by assuming the specific heat of urea at 20° C. to hold for both solid and molten urea, and by taking the heat of solution of urea at infinite dilution equal to its heat of fusion, with which it is thermodynamically equivalent provided Raoult's law of vapor pressure lowering is valid for low concentrations of urea. The following equations may be utilized to obtain the heat of reaction at 25° C.:



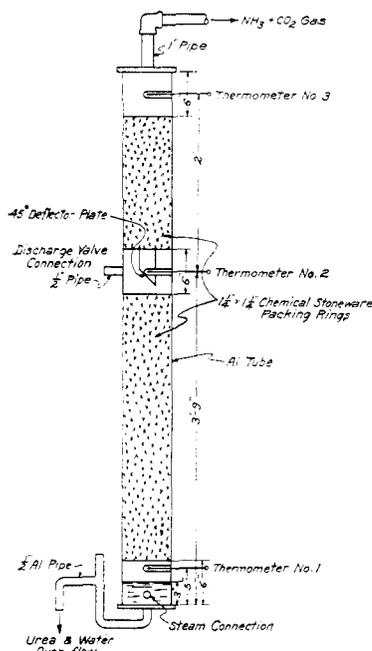


Figure 9—Urea Still

ammonia absorption tower, in which the ammonia was collected by a stream of cold water. Analysis of this scrubbing water and of urea solution discharged from the still provided a check on the nitrogen balance.

Operation of Autoclave

The performance of the autoclave has been studied by numerous experimental runs ranging in length from 3 to 7 hours each. The rates of input of ammonia and carbon diox-

ide, as well as the applied steam pressure, have been varied through wide ranges. The conditions most generally imposed have been an operating pressure of 100 to 110 atmospheres, a steam pressure of 60 pounds gage (153° C.), and inputs of 10.4 and 13.5 pounds per hour of ammonia and carbon dioxide, respectively. Conversion of the reactants to urea in these cases has been in the neighborhood of 35 to 37 per cent. The solution discharging from the still at temperatures close to 100° C. contained only small amounts of dissolved ammonia and carbon dioxide, and ranged in concentration from 35 to 40 per cent urea by weight.

The discharge from the top of the still would, when operating according to the flow sheet in Figure 1, go to the regenerator, where the ammonia would be absorbed and the carbon dioxide recovered. However, for the purposes of readily obtaining data on the autoclave performance, the mixture of ammonia and carbon dioxide was passed directly into an

ammonia absorption tower, in which the ammonia was collected by a stream of cold water. Analysis of this scrubbing water and of urea solution discharged from the still provided a check on the nitrogen balance.

The autoclave has been observed to require less steam during operation than is required to maintain it in a non-operative condition. This is in agreement with the sign, at least, of the previously calculated over-all heat effect. The actual heat requirements of the autoclave and the temperature distribution throughout the reacting mass are now being determined.

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Particle Size as a Factor in the Corrosion of Lead by Soils¹

R. M. Burns and D. J. Salley

BELL TELEPHONE LABORATORIES, 463 WEST ST., NEW YORK, N. Y.

In order to determine that part which particle size plays in the corrosion of lead by soils, lead specimens were buried in sands (generally inert in character) of various particle sizes and were maintained for periods of time ranging from 8 days to 5 months at 40° C. in a closed system in which the humidity and the composition of the atmosphere were controlled.

It has been shown that lead is corroded by contact with moist inert sands in the presence of air, and that the rate of attack is increased by increasing within certain limits

the particle size of the sand, the moisture content of the sand, and the oxygen content of the atmosphere.

Corrosion is caused by oxygen concentration cells which are set up as a result of the partial or complete exclusion of oxygen at the points of contact of metal and soil.

Soil particle size influences the rate of corrosion by determining the extent of the electrode areas, and therefore the degree of cathodic polarization, of these oxygen concentration cells.

LEAD or lead-alloy cable sheath, when buried in direct contact with soils, is often seriously corroded in a relatively short time (1, 2). The corrosion is characterized by the formation of pits which in time tend to perforate the sheath. On the other hand, when underground cables are placed in conduit, as is the standard practice, corrosion of the sheath by soils is not a serious problem even though soil waters containing soil in suspension may, and in many installations do, seep into the cable compartment.

¹ Received December 31, 1929.

It seemed probable that the essential difference in the two exposures lies in the fact that cables buried in the soil are often in direct contact with larger particles or aggregates of soil than cables in conduit, which are exposed either to soil water alone or to finely divided soil such as a deposit of silt. In the direct burial installation the presence of large particles at the surface of the sheath results in a more pronounced discontinuity of contact, while in the case of installation in conduit the water or the uniform layer of fine soil deposited from water provides a comparatively homogeneous environment.