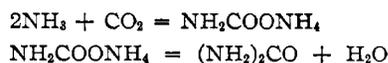# Thermal Requirements and Operating Characteristics of the Urea Autoclave[1]

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THE future commercial use of urea, either as a fertilizer or in the manufacture of synthetic resins, will depend in a large measure upon its economic production from ammonia and carbon dioxide. Autoclaving of these materials at temperatures of 135° C. and above and at pressures in the neighborhood of 100 atmospheres results in their partial transformation to urea according to the following equations:

The thermal requirements of, and the temperature distributions within, the autoclave used for the direct synthesis of urea from liquid ammonia and liquid carbon dioxide have been determined under both operative and non-operative conditions. The over-all autoclave reaction has been shown definitely to be exothermic for 35 to 40 per cent conversion of the reactants. Data are given for the corrosion resistance of a number of metals under operative conditions.

corrosion by the reacting mixture under actual operating conditions. The present paper presents the results of several such experiments on the apparatus described above.

$$2NH_3 + CO_2 = NH_2COONH_4$$

$$NH_2COONH_4 = (NH_2)_2CO + H_2O$$

Direct Synthesis of Urea

A continuous process for the synthesis of urea from liquid ammonia and liquid carbon dioxide has been developed at this laboratory and described by Krase, Gaddy, and Clark (1). A small unit for the production of 79.5 kg. (175 pounds) of urea per day has been designed, constructed, and successfully operated. In the pilot plant the anhydrous liquids are introduced separately into the base of the lead-lined autoclave by means of single-acting hydraulic-type pumps actuated by a common crankshaft. (Figure 1) The liquid ammonia is supplied directly to the pump from commercial containers. The liquid carbon dioxide usually requires preliminary drying, since in many cases it contains sufficient water to interfere with pumping. The drying is accomplished by passing the expanded gas through concentrated sulfuric acid and through wood charcoal. The carbon dioxide drying, compressing, liquefying, and storage units are shown in Figure 2. The converted mixture discharging from the top of the autoclave enters a still, where thermal decomposition of the unconverted carbon dioxide compounds of ammonia is effected. The urea is removed in aqueous solution while the ammonia and carbon dioxide pass to a regenerative system for separate recovery. The urea autoclave and still are shown in Figure 3. Introduction of the reactants at the base and withdrawal of the products at the top of the autoclave allow advantage to be taken not only of the decrease in density accompanying conversion but also of the increased efficiency of conversion to be expected by maximum loading density (2).

Scope of Present Work

Because of the almost complete absence of reliable data for estimating the over-all thermal requirements of the autoclave reactions, it seemed advisable to measure as accurately as possible in the pilot plant the heat change involved. With this information and with the available data on the heat losses through commercial autoclave lagging, the prospective manufacturer can readily calculate his steam cost for this part of the process. For the proper design of larger units it is also important to know something of the temperatures produced within the autoclave and of the resistance of commercially available alloys to the combined effect of erosion and

Experimental Procedure

The following method was employed for obtaining the energy requirements of the autoclave. With the autoclave filled with a mixture which had previously been brought to equilibrium at 153° C., ammonia and carbon dioxide were introduced in the molecular ratio of $2NH_3$ to CO_2, and the products withdrawn as in ordinary operation. Two rates of input corresponding to reaction periods of 2.31 and 1.83 hours, respectively, based on stream-line flow, and equivalent to the introduction of 110 and 139 gram-mols of carbamate per hour (200 and 250 pounds of NH_3 per 24 hours) were used in these experiments. After a steady condition had been reached, the energy consumption required to maintain the autoclave at 153° C. was determined. A blank or non-operative run was then made under the same conditions as before, except that no ammonia or carbon dioxide was added and no product withdrawn. This experiment measured the energy loss per unit time per degree temperature difference between the autoclave and the surrounding air due to convection, radiation, etc. From these data the heat evolved or absorbed per unit weight of urea produced was calculated.

Exclusive of the autoclave reactions heat was supplied to the autoclave by electric resistance coils about the mercury trap between the gage and autoclave and about the discharge valve, as well as by the steam jacket surrounding the autoclave. The steam jacket welded on the outside of the autoclave and the small steam port employed for heating the top head were connected in series. The discharge valve was heated externally to prevent freezing of the discharge port by the rapidly expanding gases passing through the outlet. The mercury trap inserted between the Bourdon tube of the autoclave gage and the autoclave head was heated to prevent solidification of the autoclave products.

For the purpose of measuring the heat consumption of the autoclave the temperature and quality of the incoming steam and the temperature and amount of the condensate discharged were determined. The quality of the steam was obtained by means of a throttling calorimeter. The energy consumed in the electrical heaters was determined separately for the discharge valve and the autoclave gage from wattmeter readings. The air temperature surrounding the autoclave was also recorded. Quite satisfactory results have been obtained in spite of several unavoidable but complicating factors, such as variations in the humidity and in the velocity of the surrounding air.

In operative runs it sufficed for the present purpose to weigh the reactants introduced into the autoclave and to determine the urea produced from the weight and analysis of the urea solution discharged at the base of the still. The unconverted carbon dioxide compounds of ammonia were vaporized by steam introduced directly into the urea solution on the base

plate of the urea still. This solution, in general discharging at about 100° C., contained from 35 to 40 per cent of urea by weight, with only negligible quantities of ammonia and carbon dioxide. In commercial practice it will probably be found more economical to operate this still under pressure without the direct introduction of steam to the mixture.
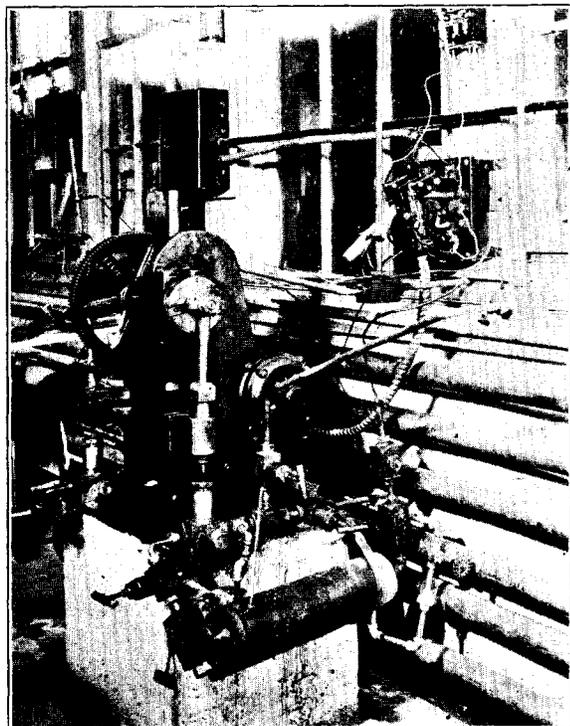

Figure 1—Liquid Ammonia and Carbon Dioxide Pumps

The urea could then be recovered in a molten condition. Davis and co-workers at this laboratory are at present engaged in obtaining equilibrium data that will be valuable in the proper design of such a recovery system.

The temperature distribution within the autoclave was determined by means of four No. 22-gage chromel-alumel thermocouples insulated from each other by close-fitting thin-walled glass tubes, the whole inserted in a thermocouple well constructed of 1.4-cm. o.d. and 0.6 cm. i.d. high-pressure steel tubing protected from corrosion by a 0.3 cm. lead coating. The thermocouple well extended through the top head of the autoclave and to within 1.9 cm. of the base. The thermocouple assembly with junctions 51.4 cm. apart could be raised or lowered at will, thus permitting determination of the temperatures at all points throughout the length of the autoclave.

A few of the metals which had been shown by the work of Thompson, Krase, and Clark (3) to be most corrosion-resistant to this system under static conditions, together with a few additional samples, were prepared for testing under actual operating conditions. These samples were drilled and mounted on a 0.3-cm. glass rod, with 0.6-cm. lengths of 0.9-cm. glass tubing separating them. Duplicate sets of samples were placed within the autoclave, near the top and bottom, respectively, and were supported by but were not in contact with the thermocouple well. This was accomplished by means of glass supports secured with lead wire.

Thermal Requirements of Autoclave

The mean values of the hourly heat losses obtained on two different non-operative runs of 3 and 4 hours each are shown

in Table I. The mean of these values is 7.25 kg-cal. per hour per degree Centigrade temperature difference between the applied steam temperature and the average surrounding air temperature. The average deviation from the mean is 0.25 kg-cal., or 3.4 per cent.

Table I—Heat Consumption of Urea Autoclave. Non-Operative Experiments

EXPERIMENT	TEMPERATURE DIFFERENCE	HEAT CONSUMPTION	
	° C.	Kg-cal./hour	Kg-cal./hour/° C.
2	149.0	1106.6	7.43
	147.7	1068.5	7.23
	146.6	1125.5	7.68
	146.1	1100.3	7.53
4	144.8	1047.9	7.24
	143.1	941.4	6.58
	142.0	1005.6	7.08
		Mean	7.25

Table II—Heat Consumption of Urea Autoclave. Operative Experiments

EXPERIMENT	TEMPERATURE DIFFERENCE	HEAT CONSUMPTION	UREA PRODUCED	CONVERSION	HEAT OF REACTION
	° C.	Kg-cal./hour	Kg./hour	%	Kg-cal./kg. urea
1	156.1	781.7	3.20	35.5	109.4
	155.6	732.6	3.30	40.2	119.8
	155.1	729.6	2.98	36.4	132.5
3	135.8	570.5	3.13	36.3	132.3
	133.6	550.6	3.06	36.4	136.6
	132.4	560.5	3.05	36.3	131.0
	132.2	535.5	2.99	34.7	141.5
	132.4	547.4	3.07	34.9	134.4
5	135.5	728.5	2.33	36.7	109.0
	134.3	691.1	2.37	34.9	119.2
	133.8	656.2	2.47	35.2	127.1
	132.5	621.4	2.49	40.1	136.2
	132.1	608.4	2.54	37.3	137.5
				Mean 36.5	128.2

During operative runs the heat consumption of the autoclave was considerably less than in non-operative runs. Applying the mean value of the heat consumption per degree Centigrade temperature difference to the data of the operative runs and referring the heat evolved to the weight of urea produced, the values given in Table II are obtained. Here the mean value of the heat evolved per kilogram of urea formed is 128.2 kg-cal. at 36.5 per cent conversion with an average deviation from the mean of 8.7 kg-cal., or 6.8 per cent. This
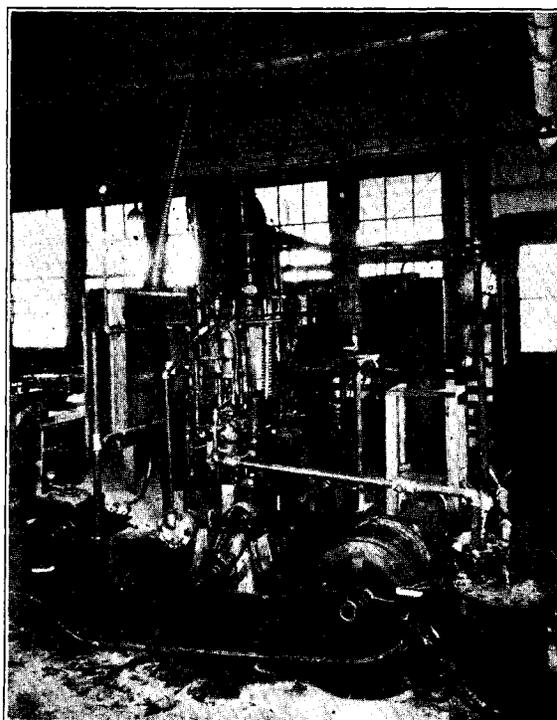

Figure 2—Carbon Dioxide Drying, Compressing, Liquefying, and Storage Units

mean value of 128.2 kg-cal. is equivalent to an evolution of 7700 gram-calories per gram-mol of urea produced at 36.5 per cent conversion from the reactants at 4.5° C. and 110 atmospheres pressure to the final state of the conversion mixture discharged from the autoclave at 65° C. and 1 atmosphere pressure.

Figure 3—Urea Autoclave and Still

Temperature Distribution within Autoclave

The temperature distributions throughout the autoclave during both blank and operative runs are compared with the applied temperature in Figure 4. During blank runs the temperature at the base of the autoclave was 146.5° C., or 5 degrees below the temperature of the remainder of the autoclave. This effect was due to conduction through the mountings and to radiation from the lower head which, although well lagged, was not provided with steam ports. In the operative runs the uniformity of temperature throughout the autoclave (166.8° to 168.6° C.) may be an indication of turbulent flow. The mean temperature of the reactants was 168.1° C., or 15 degrees above the applied temperature, indicating a strongly exothermic reaction.

Heat of Autoclave Reactions

An over-all hourly heat balance for the autoclave reactions may now be set up by the same method as that employed by Krase, Gaddy, and Clark (1), except that the proper corrections for the actually determined temperature of reaction and percentage conversion of the reactants may be included. If this is done, the over-all heat balance obtained for an input of 139 gram-mols of carbon dioxide is as shown in Table III.

In order to make a comparison between the calculated value of the reactions and the experimentally determined heat requirement of the autoclave, it is necessary to correct the latter for the heat change accompanying the change in state of the products from 168.5° C. and 110 atmospheres to 65° C. and 1 atmosphere. The heat change accompanying the discharge of the products from 168.5° C. and 110 atmospheres

to 65° C. and 1 atmosphere is measured by the difference between the energy requirements of the discharge valve in operating and in non-operating runs. The real difference in energy requirements of the discharge valve cannot be measured directly, since heat is supplied to it both by an electrical resistance coil and by conduction from the autoclave. Experimentally, that portion of the energy increase supplied by the resistance coil was found to have a mean value of 51.0 kg-cal. per hour per kilogram of urea produced. If, as seems very probable, at least half the additional energy is supplied by the resistance coil, then the actual value of the total increase in energy requirements lies between 51.0 and 102.0 kg-cal. per hour and may be assumed to be 76.5 ± 25.5 kg-cal. per hour. The heat evolved in the formation of 1 kg. of urea then becomes 128.2 + 76.5 ± 25.5, or 204.7 ± 25.5 kg-cal., which is equivalent to 623 ± 78 kg-cal. for the net over-all liberation of heat within the autoclave for 36.5 per cent conversion of 139 gram-mols of carbon dioxide to urea. This result indicates that the calculated heat effect of 705 kg-cal. is close to the true value.

Table III—Over-All Hourly Heat Balance

	Kg-cal.
Heat liberated in autoclave:	
Formation of 139 gram-mols of ammonium carbamate...	5290
Conversion of 0.365 × 139 gram-mols carbamate to urea. .	400
Heat absorbed in autoclave:	
Heat necessary for evaporating 278 gram-mols of NH₃ and heating to 25° C.	1425
Heat necessary for evaporating 139 gram-mols of CO₂ and heating to 25° C.	265
Heating 139 gram-mols of carbamate from 25° to 168.5° C.	725
Heat of fusion of 139 gram-mols of carbamate..........	2570
Net over-all heat liberated...........................	705

Autoclave Operation without Steam

A later experiment was carried out in which the conditions of operation imposed in the above experiments were maintained except that after operation had been initiated no steam was supplied to the autoclave. Owing to the additional insulating effect of the steam jacket, the total heat requirement was only 81.5 per cent of that required in previous runs. The autoclave operated at an average temperature of 165° C. and at a slightly lower conversion efficiency. The energy distribution between the various sources for the two methods of operation is compared in Table IV.

Table IV—Distribution of the Energy Requirements in Operative Experiments

SOURCE	NORMAL OPERATION %	WITHOUT STEAM %
Steam	38.0	...
Gage heater	6.5	11.5
Valve heater	23.5	38.5
Reaction	32.0	50.0

Table V—Results of Corrosion Tests

SAMPLE	NON-FERROUS COMPOSITION				Loss	RELATIVE PENETRATION
	C %	Cr %	Ni %	Si %	Mg./sq. cm.	
1 Chromium					0.21 gain	0
2 Tantalum					0.10 gain	0
3 Duriron				14.5	2.4	1.0
4 Nickel					13.2	4.3
5 Illium G	0.5	21.5	58.5	1.4	12.5	4.4
6 Rezistal 4	0.23	18	22.5	2.9	37.0	13.9
7 Lead					67.4	17.3
8 Aluminum					55.4	59.9
9 Enduro KA 2	0.15	18.0	8.5	<0.75	308.0	114.3
10 Tin					506.0	252.1
11 Zinc					Complete solution	

Results of Corrosion Tests

The metal samples placed within the autoclave for corrosion testing were subjected to non-operative conditions for about 8 hours, to operative conditions for between 20 and 25 hours, and to the periods of preliminary heating and subsequent cooling attending each experiment. Since the total corrosion is the sum of the effects of these varying conditions, the results

are expressed as relative penetration referred to the least corroded sample as unity rather than on the usual "penetration per year" basis.

UREA AUTOCLAVE TEMPERATURE DISTRIBUTION
(1) Applied Steam Temperature
(2) Non-Operative Run Temperature
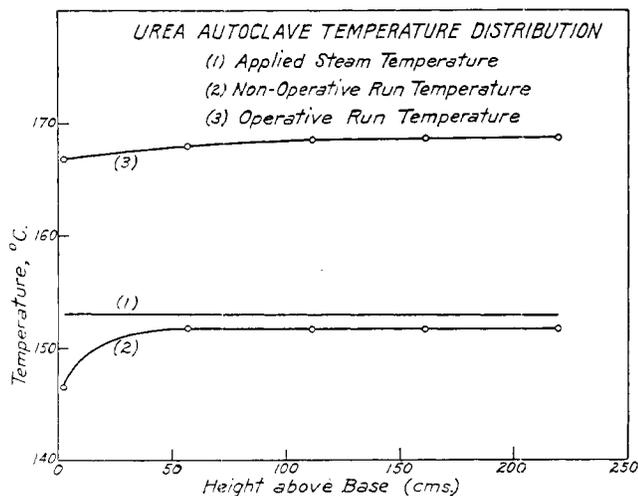(3) Operative Run Temperature

Figure 4

A comparison of these results with those obtained by Thompson, Krase, and Clark (3) indicates in a few cases a reversal in the relative resistance to corrosion under the more exacting requirements of actual operating conditions. In general the most corrosion-resistant alloys appear to be high-silicon chrome-nickel steels.

Autoclave Efficiency

No reliable conversion data for the urea-water-carbamate system have been published for temperatures above 155° C. The yields of urea in this system at temperatures above 150° C. are now being determined at this laboratory. The preliminary and unpublished results indicate the equilibrium at 170° C. to correspond to 47.8 per cent conversion to urea. Comparison of this value with the autoclave performance without respect to the reaction period allowed gives an operating efficiency of $\dfrac{36.5 \times 100}{47.8}$, or 76 per cent.

Conclusions

The over-all autoclave reaction has been established as being strongly exothermic both from the calculated over-all heat balance and from the experimentally determined heat requirements of the autoclave.

Proper design of large-scale equipment will reduce the steam consumption of the autoclave to a negligible value per kilogram of urea produced.

High-silicon chrome-nickel steels offer a high degree of resistance to both erosion and corrosion by the molten mixture. They are capable of being machined, and are strong and tough enough to withstand the pressures and temperatures employed in actual working conditions.

Literature Cited

(1) Krase, Gaddy, and Clark, IND. ENG. CHEM., 22, 289 (1930).
(2) Matignon and Frejacques, Bull. soc. chim., 31, 394 (1922).
(3) Thompson, Krase, and Clark, IND. ENG. CHEM., 22, 735 (1930).

The Growing Industry—Dry-Ice[1]

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JUST as a chance grain of sand in an oyster's shell forms the starting point of a pearl, so an idea is the nucleus for industrial development. Many other factors affect both pearls and industries, but a perfect pearl grows only on the right kind of a sand grain and an industry develops to an imposing extent only if it be based on the right idea in the beginning. The industry of commercial refrigeration by solid carbon dioxide (most widely known under the trademark "Dry-Ice") admirably illustrates this thesis.

Numerous attempts to apply solid carbon dioxide to the problems of refrigeration of foodstuffs amounted to nothing in the past because, among other things, their promoters failed to realize and to take into account the peculiar problems involved in making so extraordinary and so expensive a material practically usable. In 1924, Thomas B. Slate applied for United States patents on ideas, which if one is to judge from the results, were the correct ones on which an industry could be built. Although methods of preparation of solid carbon dioxide in useful form were not neglected in Slate's applications, he placed principal emphasis on utilization of the peculiar value of this material in maintaining low temperatures, and devised methods of putting it economically to work. Others before him had been looking for a time, which so far has failed to materialize, when solid carbon dioxide could be made and sold for a price directly competitive with ice, solid water.

The wisdom of attacking the problem from Slate's angle has been borne out by the development in the intervening period of an industry of considerable proportions and by the working of a revolution in the refrigerated transportation of perishables. The first pound of solid carbon dioxide for commercial refrigerating purposes was sold by the DryIce Corporation of America in 1925. In 1929 production approached 15,000 tons, and the expected sales for the calendar year 1930, based upon figures for half of that period, will probably exceed double that figure, greater than the annual production of liquid carbon dioxide in the United States. This quantity of material is being produced in eighteen plants from coast to coast in the United States and distribution is being effected through twenty-seven sales outlets supplied from plants more or less remote by automobile truck and by a private railroad car line of forty cars devoted solely to this service. One could scarcely ask for more conclusive evidence than that under such circumstances.

Properties of Solid Carbon Dioxide

To understand this swift growth it is necessary to consider those peculiarities of solid carbon dioxide which have made its use practicable to so wide an extent. Statistically its properties are:

Specific gravity	1.56
Subliming temperature in carbon dioxide at 760 mm.	−78.6° C. (−109.6° F.)
Latent heat at subliming temperature	246 B. t. u. per lb.
Specific heat of gas (average)	0.193
Total refrigeration to 40° F.	273 B. t. u. per lb.