

GENERATION OF NITROGEN FROM UREA.

A PROJECT REPORT WRITTEN

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DEDICATION

This work is dedicated to my late Father

May his soul rest in peace 'Amen'

ABSTRACT

Crystalline urea when subjected to heat at controlled rate will release ammonia and carbon dioxide. When ammonia reacts with oxygen of the air, Nitrogen will be generated. The generated Nitrogen is necessary in INERT ATMOSPHERE FOR STORAGE. This project therefore aims at generating such nitrogen that could be used for modifying storage environment. For lack of the necessary fund and the bulk nature of designing and testing inert atmosphere. Silos to which the generated nitrogen can be channeled, this study is within the scope of only generating the Nitrogen from urea which will serve as a stepping forward in the research to construct inert atmospheric storage silos. In this research work, urea technology is highlighted as a Nitrogen source which contribute in no small measure in making our Nation of the Countries which will benefit from urea technology in the World.

ACKNOWLEDGEMENT

I am sincerely grateful to almighty ALLAH for seeing me through all odds and obstacles I have encountered during the period of my studies. I must confess that I have done nothing of my own strength. He actually did everything for me.

Also, I am grateful to my parents for their both moral and financial support ever since I started my school up to this period.

My thanks goes to my supervisor Mr ONUACHU A.C. for finding time to go through this work and making useful comments and suggestions. I will not forget to register my appreciation to the entire members of Staff for their selfless services!

My profound gratitude goes to KODO SAIDOU for his kind and cooperation for sparing his time to type this project for me as required.

Lastly I will not forget to express my sincere thanks to those I will like to call my Country people, my friends indeed and not in need. I would like to thank all of them, but due to lack of space and time I will just say:

THANKS, GOD PROTECTION AND BLESSING ON ALL "AMEN".

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NOTATIONS AND SYMBOLS

1. Ba ----- Barium
2. Br ----- Bromine
3. C ----- Carbon
4. Ca ----- Calcium
5. Cl ----- Chlorine
6. Cr ----- Chromium
7. H ----- Hydrogen
8. Mg ----- Magnesium
9. Na ----- Sodium
10. O ----- Oxygen

SYMBOLS FOR COMPOUNDS

11. $\text{Ba}(\text{N}_3)_2$ -----> Barium azide
12. $\text{Ca}(\text{OCl})_2$ -----> Calcium hypochlorite
13. CrO_3 -----> Chromic oxide
14. $\text{CO}(\text{NH}_2)_2$ -----> Carbamide (urea)
15. CO_2 -----> Carbondioxide
16. HCl -----> Hydrochloric acid
17. H_2O -----> Water
18. Mg_3N_2 -----> Magnesium nitrite
19. NaOBr -----> Sodium hypobromite
20. NH_3 -----> Ammonia
21. $(\text{NH}_4)_2\text{CrO}_7$ -----> Ammonium dichromate

22. $(\text{NH}_4)_2\text{CO}_3$ -----> Ammonium carbonate
23. NH_4NO_2 -----> Ammonium nitrite
24. NH_4Cl -----> Ammonium chloride
25. N_2H_4 -----> Hydrazide
26. NO_2 -----> Nitric oxide
27. ΔH^0 -----> Enthalpy (25°C)
28. ΔG^0 -----> Free Energy (25°C)

1.0 INTRODUCTION

In the past the African man lived on subsistence farming and hardly could he produce surplus. But nowadays, to prevent hunger due to drought or other calamities and with the improved agricultural technology, crops are produced to make provision over one year. Hence the necessity of storing the surplus crops. This storage implies safe keeping conditions of crop, many problems led to crops storage among which we can mention spoilage due to high moisture content of grains. In order to prevent this problems (spoilage).

Researches have been conducted by many researchers. Therefore the techniques of using an inert storage environment were found. In this project we are making of Nitrogen to form the inert environment, as Nitrogen an inert gas. Due to that fact, there is a crucial need to produce Nitrogen which will be applied to the storage environment. But due to lack of fund and time, the purpose of this project will consist of generation of Nitrogen from urea fertilizer (inorganic matter) which will be applied to the storage environment in further studies.

1.1 JUSTIFICATION AND NATURE OF THE PROBLEM

The importance of maize as a staple food crop in Nigeria both for human consumption and for livestock feeds cannot be over emphasized. In Nigeria it was reported out of 8.062 million tons of grains produced in 1975 (F.A.O production year book) 1 million tons was maize.) In 1984, the level of annual production of maize 1.171 million domestic consumption required as being short of minimum domestic consumption requirement by about 48.9% Since then a lot of efforts has been made to gear up maize production to meet up the consumption requirement through the work of the eleven river basic and rural development Authority, the Nigeria National Grains Board, the Federal Department of Agriculture and Nation resources through world Bank project of Agriculture Development project and the private farmer, all helping in seeing to it that Nigeria achieves the national goal of self efficiency and self reliant in maize food production and agrobased industrial raw materials. In view of this situation, it is envisaged that a point will be reached when maize production will increase to such an extent that we have to find alternative ways of storing excess maize produced.

It is a known fact high moisture corn storage poses a complex problem to the agricultural scientists and Engineers in related field. A few of those factor responsible for high

moisture being a **problem** include date of harvest, initial moisture content, grains temperature and whether conditions.

The main crop is harvested in August and September each year and light crop in December. The maize is usually stored on the cob by farmers while some quantity is shelled immediately after harvest for sale. Crops harvested during rainy season have high moisture content at the harvest: about 35%, wet basis (wb) for kernels and 40 - 50% (wb) were quoted by Anazodo (1977) for cob. Storing of the maize grains under these fresh conditions for maize shelled immediately after harvest without further drying adds more to the risk of mould deterioration as shown by studies carried out by Broad bent (1967), Oyeniran (1973). The traditional method of crib- storage has in recent years been improved by the introduction of the modern crib for maize farmers' designed by the Nigeria Stored Products Research Institute. This method has the advantage of reducing the chance of mould infection of the maize by the fact that the moisture content of maize being stored is gradually but effectively reduced as soon as storage in the crib commences. Moreover, maize on the cob is less prone to mould attack as long as the grains are attached to the rachis is observed in wheat by Christenson (1957). However, in practice this result is not often obtained.

In view of the problems associated with maize storage either

encouraged and moulds inhibited as O_2 was decreased and CO_2 increased.

A number of chemicals have been evaluated as grain mould inhibitors. Most of the work has been conducted with the intention of using high moisture grain as livestock feed. The chemicals used were mostly organic acids or mixtures of organic acids (Hall, et al 1974; Sauer and Burroughs 1974; Sauer et al 1975). Ammonia has also been successfully used by some scientists (Bothast et al 1973; Lancaster et al 1977) used gaseous ammonia in ambient air drying of high- moisture corn to retard mould growth.

In the light of all the above mentioned studies, the present study therefore aims at trying to use an alternative, cheaper and far less dangerous source of ammonia cum nitrogen than use of above named somewhat toxic and dangerous chemicals. This alternative method involves the use of urea as a source of Nitrogen. When Nitrogen is generated and source, it could be used for modifying storage environment. In this study therefore crystalline urea reacts in solution as heat is applied to release ammonia which in turn reacts with Oxygen of the air to give nitrogen. Urea contains 45 - 46% by weight of nitrogen.

With the scope of this study, nitrogen will be generated but

further research work could be carried out to design and construct inert atmosphere silos. This will enable us to test the use of generated nitrogen channeled into the silos fabricated of metal but made completely air tight. The top of which is provided with strong projections on which ordinary palm fronds are appropriately arranged and strongly tied together to provide a cheaper shade. The silo should be provided with an opening on the top, cone which is used for loading the silo with grains by the use of anger or conveyor. The inert silo is provided with a rubber padded gasket to provide air tightness when closed. Similarly, an outlet for emptying the silo is provided with a ted with rubber - padded gasket. The silos have a link up with a system of gas pipes which is used to introduce gas into the silos. Grains are loaded to fill the silos completely by the use of anger or conveyor. The gas inlet pipe is connected to a source of nitrogen (an inert gas) generated from urea and the gas outlet pipe is used to evaluate the air originally in the silo. The air in the silo which normally contains Oxygen is purged out by replacing it with nitrogen until full replacement is achieved. The inlet and the outlet pipes are connected to pressostate and valves which allow more gas into the silo automatically when the need arises. The grains now in inert atmosphere are kept in good condition for a very long time.

The Nitrogen Stored Products Research Institute has

1.2 OBJECTIVES AND SCOPE OF STUDY

The above thoughts led to the following objectives:

- (1) To determine the applicability of using urea as a source of nitrogen generation.
- (2) To determine the possibility of generating ammonia from urea through heat application which in turn reacts with ambient air to release Nitrogen as inert gas for modifying storage environment.
- (3) To obtain results from experiments which would be subjected to statistical analysis using experiment design.
- (4) To obtain quantifiable Nitrogen which in the course of further research work would be used in modifying storage environment.

In carrying out this project work, the scope is being limited to use of urea as the source of Nitrogen generation. In view of the financial involvement and time factor, a further research need to be carried out to channel the generated Nitrogen into silo or bin or even crib to modify the storage environment. This project should be viewed with interest as a commercial venture, the scope of which when emphasized, the study should be encouraged as it could lead to the modification of the existing storage cribs or silos or bin by incorporating control valves through which the Nitrogen

generated from urea will be introduced into the wet corn under storage with a view to reducing the present exorbitant cost of dryers which only dry the corn to safe storage moisture content and later to be stored in a silo or bin.

But with the present study when successfully executed will be of advantage since farmers will harvest early and store directly in cribs, bins or silos and with Nitrogen supplied, the storage environment is modified thereby reducing cost of buying separate dryers and storage bins or silos.

CHAPTER TWO

LITERATURE REVIEW

2.1 HISTORICAL BACKGROUND OF NITROGEN AS AN INERT GAS

In 1772 Daniel Rutherford allowed Mice to breath in air under a bell- jar and removed the fixed air (CO_2) by washing the residual gas with caustic potash solution. A gas remained which did not support combustion or respiration but unlike fixed air, was not absorbed by alkali or lime- water. Priestley (1772) burnt charcoal in a confined volume of air and absorbed the fixed air with alkali, also obtaining a "mephitic air" which he called phlogisticated air. Both considered that the gas was common air saturated with phlogiston emitted by the animal or combustible body. Scheele (1772) proved air is a mixture of two gases, fire air which supports combustion and respiration, and foul air which does not. Lavoisier (1775 - 1794) gave a decisive proof of this, and called Scheele's gas azote (Greek a, no, Zōē, life), a name still used in France, the name Nitrogen (Greek nitron, nitre) was suggested by Berthollet in 1790.

Atmospheric Nitrogen was considered to be a pure substance until in 1894 Rayleigh and Ramsay found that it contains rather more than 1 percent by weight of an inert gas which unlike Nitrogen does not combine with heated Magnesium. The inert gas, existence of which had been indicated by Cavendish in 1785, was called argon (Greek argon, sluggish); later experiments by Ramsay and Travers showed that the atmosphere contains traces of other inert gases: Helium, Neon, Krypton and Xenon.

The composition of air freed from moisture and carbon dioxide is roughly 4 volume of Nitrogen to 1 volume of Oxygen, the Exact figures (Leduc, 1896) are:

	By weight	By volume
Nitrogen	75.5	78.06
Oxygen	23.2	21.00
Argon	1.3	0.94

The very early constant composition of dry atmospheric air was proved by Cavendish in 1783 (20.833 vol of Oxygen and 79.167 vol of Nitrogen and argon). Benedict (1912) and Carpenter (1937) found that the volume percentages of Oxygen (20.939) and carbon dioxide (0.031) in uncontaminated air are very constant.

2.2 CHEMISTRY AND METHODS OF NITROGEN PRODUCTION

2.2.1 PREPARATION FROM THE ATMOSPHERE

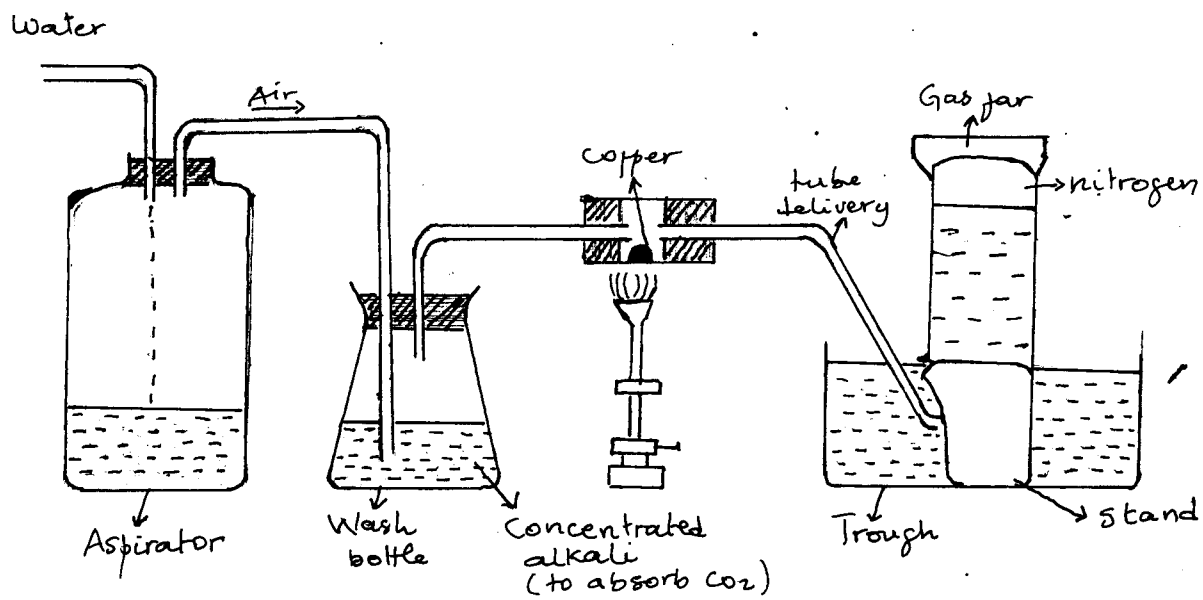


Fig1: Preparation of Nitrogen from the atmosphere

Water enters an aspirator (fig1) and pushes air out. The air passes through a concentrated solution of alkali (caustic soda or caustic potash) to remove carbon Oxide. The air then passes over heated copper to remove Oxygen. Nitrogen remains and is collected over water. If a dry specimen of gas is wanted, the gas is passed a U- tube containing glass beads wetted with concentrated Sulfuric acid. This dries the gas and it is then collected over mercury.

2.2.2 COMMERCIAL PREPARATION OF NITROGEN

Atmospheric air is filtered to remove dust, and then compressed to a high pressure (about 200 atmosphere). The compression heats the air, so the air is passed through water cooled tubes to remove the heat. The compressed air is next passed through a fine jet into an expansion chamber. The sudden expansion makes the air very cold. This cold air is used to cool the air coming into the expansion chamber. Successive cooling makes the air cold enough to liquefy it. Liquid air is then passed into a fractionating column. Nitrogen boils off first at minus 196°) and Oxygen after at minus 183°). Liquid air cools the gases as they boil off and condenses them to liquids(fig2)

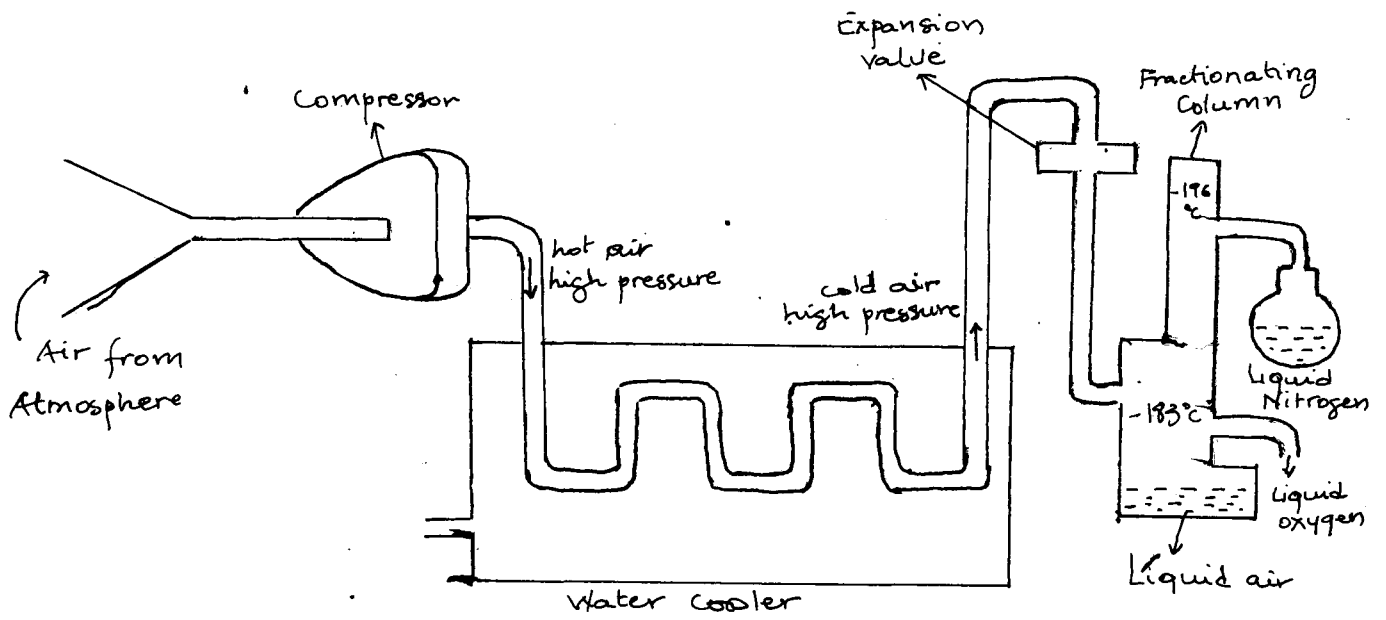
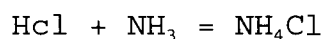
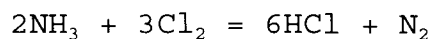


Fig2: Preparation of Nitrogen from Compounds

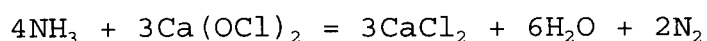
Nitrogen is prepared in the Laboratory by methods mostly depending on the oxidation of ammonia, the hydrogen being removed and the Nitrogen set free.

1. When chlorine gas is passed into, or bromine is added to, concentrated ammonia solution, nitrogen is evolved

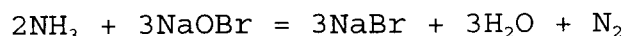


The reaction with bromine being similar caution: in the case of chlorine the reaction is vigorous, flashes if light being seen in a darkened room: care should be taken to keep the ammonia in excess otherwise the very explosive liquid nitrogen trichloride NCl_3 is formed

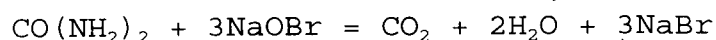
2. Instead of free chlorine, a thin paste of 40gm of bleaching powder containing Calcium hypochlorite $\text{Ca}(\text{OCl})_2$ may be run through a thistle funnel into 100ml of concentrated ammonia solution warmed in a flask (explosions have been reported).



Instead of bromine, sodium hypobromite solution (6ml of bromine freshly dissolved in a cold solution of 10gm of sodium hydroxide in 100ml of water is dropped into concentrated ammonia solution:

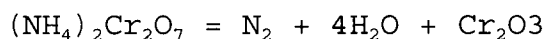


Nitrogen is also evolved by the action of alkaline hypobromite solution on urea.

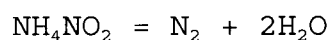


This gas contains a trace of Nitrous oxide N_2O which is removed by passing over red-hot coals.

3. When heated crystals of ammonium dichromate are gently heated they decompose violently with flashes of light, Nitrogen and steam are evolved and a voluminous green residue of chromic oxide left

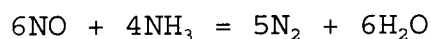


4. The most convenient method of preparing Nitrogen is to heat a solution containing ammonium nitrite made by dissolving equimolecular amounts of sodium nitrite and ammonium chloride or sulphate in water:

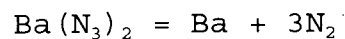


The gas evolved is washed with dilute sulfuric acid to remove ammonia, and collected over water.

5. Pure Nitrogen is obtained by passing a mixture of nitric oxide and ammonia gas over red-hot copper



6. Very pure Nitrogen is evolved on heating barium azide in an evacuated apparatus



This preparation does not involve (an oxidation of ammonia)

Nitrogen gas may be dried by calcium chloride, concentrated sulfuric acid or phosphorus pentoxide and collected over mercury. Compressed Nitrogen in grey cylinders may be brought; it usually contains a little Oxygen which may be

taken out by passing over copper turnings heated to bright redness.

2.3 PROPERTIES OF NITROGEN

2.3.1 PHYSICAL PROPERTIES

1. It is a colourless, odourless, tasteless gas
2. It is slightly less dense than air, normal density: 1.2507gm/litre. (atmospheric Nitrogen is 0.48 percent heavier)
3. It is very sparingly soluble in water (2cm³ per 100cm³ water)

2.3.2 CHEMICAL PROPERTIES

The gas is inert as it does not support combustion, does not burn and is not attacked by the usual chemical agents, it is not poisonous, it does not turn lime - water milky. It has no action on litmas. It is liquefied by cooling critical temperature:-147.13⁰

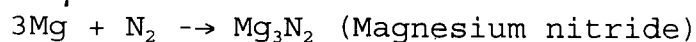
Critical pressure : 33.49 atmosphere.

The liquid Nitrogen is colourless, boilage point -195.81⁰C, density at boiling point 0.8042 and on rapid evaporation under reduced pressure it forms a colourless ice- like soiled.

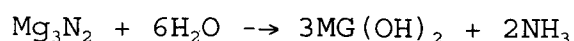
Melting point: -210.5⁰/86mm.

The gas will combine with heated metals, a nitride is formed.

When Magnesium ribbon is burnt in a crucible. The oxide is formed and some nitride as well.



Nitrides are readily composed by water to give ammonia; so few drops of water are put in the crucible and ammonia is given off.



Chemical test:

The gas extinguishes a lighted splint. To distinguish the gas from carbon dioxide, pass it into lime water. Nitrogen has no effect on lime-water.

2.4 APPLICATION OF NITROGEN

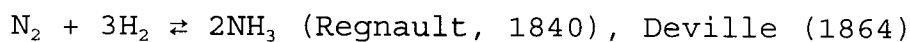
Nitrogen forms three well defined compounds with hydrogen: ammonia (NH_3), hydrazide N_2H_4 , and hydrazoic acid N_3H .

Ammonia and hydrazide are basic substances combining with acids to form ammonium and hydrazide salts; e.g.: NH_3 , HCl or NH_4Cl , HCl or $\text{N}_2\text{H}_5\text{Cl}$ and N_2H_4 , 2HCl or $\text{N}_2\text{H}_6\text{Cl}_2$. Part of the hydrogen of ammonia and hydrazide may, however, be replaced by alkali metals forming e.g.: NaNH_2 and H_2N , NHNa .

Hydrazoic acid is an acid, dissolving metals and forming

salts eg.: NaN_3 . It combines with ammonia and with hydrazide to form the compounds NH_4N_3 (or N_4H_4) and $\text{N}_2\text{H}_5\text{N}_3$ (or N_5H_5) respectively. The ion N_3 is univalent.

Nitrogen when sparked with hydrogen forms ammonia

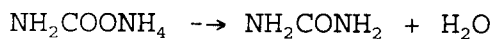
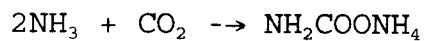


pointed out that electric sparks both form and decompose ammonia. The reaction is reversible and a state of equilibrium is set up in which 6 percent of NH_3 exists with 94 percent of uncombined gases.

A very important application of Nitrogen is in the inert atmospheric storage for which the project is being carried out to generate Nitrogen which as an inert gas could be used to modify storage environment.

2.5 UREA PRODUCTION AND IMPORTANCE

Urea or carbamide as it is sometimes called, is a nonionic nitrogen material used industrially in the manufacture of plastics, in fertilizers and as a protein, supplement in the feed of numinant animals. Its preparation is a bit more complicated than that of many fertilizer salts, which essentially require only the neutralization of an acid with ammonia and carbondioxide gas under very high pressure in the presence of a suitable catalyst. The reactions are represented in the following equations:



↑
Urea

Fertilizer grade urea is a water soluble acid forming material containing about 45 percent nitrogen. When conditioned, it is non caking and free - flowing, which are excellent storage and handling qualities. Urea has many applications and for that reason its supply for use in fertilizer tends to be limited.

In the current round of N, capacity expansions, urea has been of primary importance. It is expanding faster than any of the other N products, especially in the developing regions.

Table 1 below shows urea's share of the total market in 1967 and 1970, with estimates for 1975. Note that the developing countries of Asia were to be major producing countries by 1975, with over 4.6 million metric tons of N capacity. This region would rely heavily on urea.

Region	Urea capacity and % of total N capacity		
	1967	1970	1975
	Million metric ton of N		
North America	1.49 (14.2%)	2.14 (15.4%)	2.26 (15.4%)
Western Europe	1.29 (12.3%)	2.46 (17.1%)	2.85 (18.8%)
Japan & Oceania	0.99 (40%)	1.56 (43.2%)	1.94 (42.4%)
Asia *	0.83 (44.8%)	2.06 (57.6%)	4.62 (65.7%)
Latin America	0.17 (16.0%)	0.37 (19.7%)	1.21 (39.9%)

* Excludes Japan and Communist Asia

As its primary N source since urea capacity in 1975 will represent more than 65% of the total N capacity for the region Latin America also were expected to rely heavily on urea by 1975, moving from a share of 20% to almost 40% of total capacity by 1975.

In North America and western Europe, urea capacity has increased steadily; however, very little change in the market share has taken place with rapid increase in urea exports from North America and Western Europe, it is evident that much of the production from the capacity build up between 1967 and 1970.

Urea technology has advanced rapidly in the last few years. Large production units are now common place and unit costs of production have been reduced sharply. Because urea is a

high analysis product, with relatively low unit transportation and distribution costs, plus the fact that it can be used either as a solid, or solution or as an intermediate in producing compound fertilizers, it offers obvious advantages over certain N sources.

It appears obvious that the fertilizer industry will concentrate on greatest benefits from integration of the production, transportation and marketing systems that will develop in the next decade.

PHYSICAL PROPERTIES OF UREA

NH_2CONH_2 ----- molecular formulae

60 ----- molecular weight

1.33 ----- density

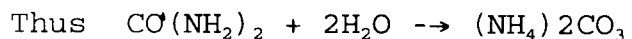
133°C ----- melting point

Urea decomposes at temperature above melting points urea is very soluble in water and its solubility in cold water in g/100g is 74 in a given temperature of water is 5°C.

2.6 PRODUCTION OF NITROGEN FROM UREA

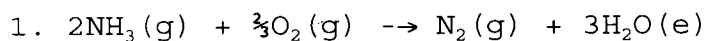
When crystalline urea is dissolved in water, the solution is ammonium carbonate which when heated yields ammonia,

carbondioxide and water



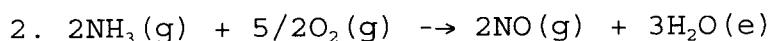
The ammonia released from the above reaction is of importance in the generation of Nitrogen. This is made possible by channeling the released ammonia into another chamber where Oxygen is introduced to react with the ammonia to give off Nitrogen.

Ammonia at room temperature is stable with respect to decomposition into N_2 and H_2 (ΔG^0 form = -4.0Kcal/mole of NH_3), however, when mixed with oxygen (or air) ammonia tends to undergo spontaneous oxidation, forming water and either NO or N_2 or both. At 25°C and 1 atmosphere we have:



$$\Delta H^0 = -182.9\text{Kcal/mol} - \text{eqn}$$

$$\Delta G^0 = -162.7\text{Kcal/mol} - \text{eqn}$$



$$\Delta H^0 = -139.7\text{Kcal/mol} - \text{eqn}$$

$$\Delta G^0 = -120.7\text{Kcal/mol} - \text{eqn}$$

As the ΔG^0 values show, both reactions are thermodynamically favourable, although the one that produces N_2 is more favourable than the one that yields NO. At room temperature both reactions take place so very slowly that no dictable amounts of the products are found, but at temperature at about $500^{\circ}C$ they proceed at an appreciable rate. If at that temperature both reactions are allowed to reach equilibrium, a greater amount of N_2 than NO will form. However by carrying out oxidation of NH_3 in the presence of a catalyst of platinum gauze, the reaction of NH_3 and O_2 yields principally NO because the platinum catalyst accelerates reaction 1 more than reaction 2. Therefore if the reaction is to favour N_2 , platinum gauze catalyst is not needed, the mixture of NH_3 and air heated to $500^{\circ}C$ under industrial set up will yield more of N_2 and the products are then cooled by passing through a condenser and separation takes place from the reaction mixture before equilibrium has time to be established.

Note that under these conditions the rate factor determines the relative quantities of NO and N_2 production rather than the free energy factor.

CHAPTER THREE

EXPERIMENTAL

3.1 TEST APPARATUS

The test apparatus used in the generation of Nitrogen for modifying storage environment is shown schematically in figure 3 while figure 4 gives a photography of the set-up while experiments are in progress.

Briefly, it consists of a heating mantle with temperature regulator, round bottom flask with three openings for thermometer inlet, separating funnel and an outlet leading out the ammonia generated. There is a delivery tube to which a mercury manometer is coupled, a reaction chamber for reduction of ammonia by oxygen of the air from an improvised car tube. A second thermometer is inverted into this reaction chamber and an inlet opening connected to a condenser through which the generated Nitrogen passes through before entering the collection tube of which a car tyre tube is improvised.

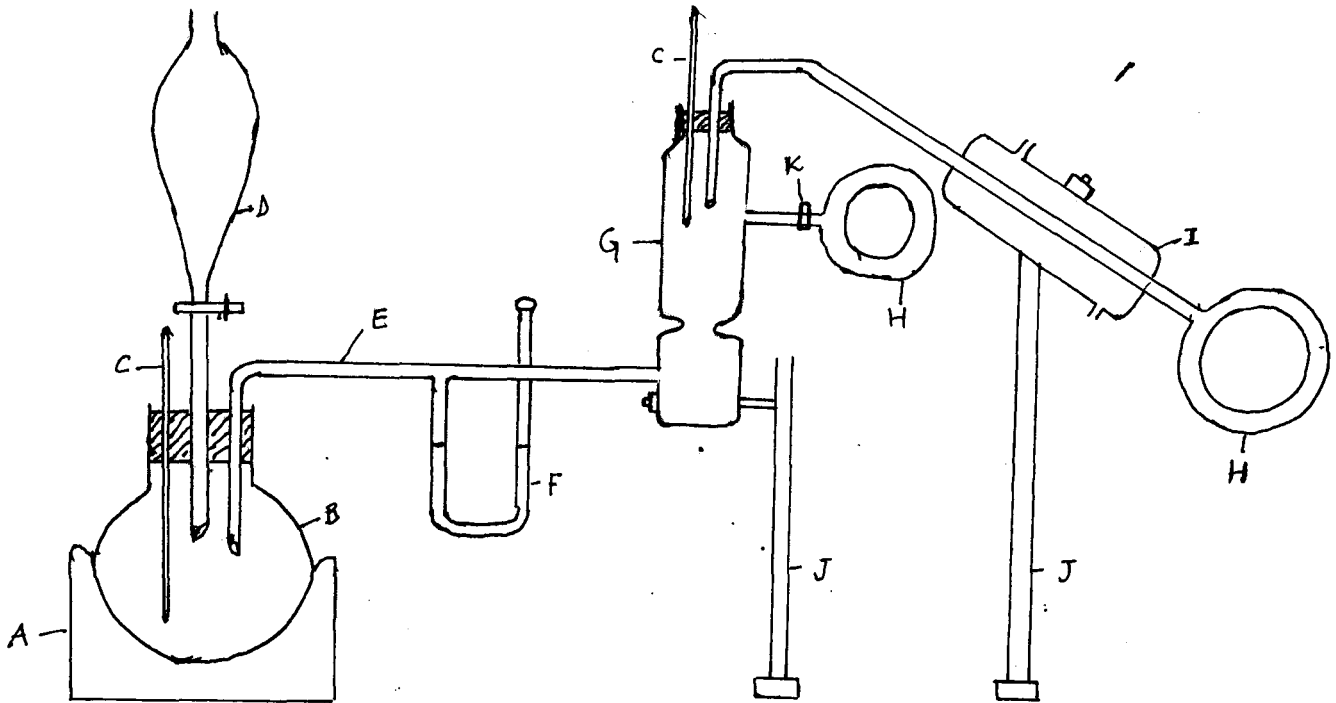


FIG. 3 SCHEMATIC DIAGRAM OF EQUIPMENT FOR THE GENERATION OF NITROGEN FOR MODIFYING STORAGE ENVIRONMENT

- A - Heating mantle
- B - Round bottom flask
- C - Thermometer
- D - Separating funnel
- E - Delivery tube
- F - Mercury in glass manometer
- G - Reduction Chamber for ammonia
- H - Tyre tube
- I - Condenser
- J - Clamp stand
- K - Clips

fig A Photograph of the set up of the apparatus for the generation of nitrogen from Urea fertilizer for modifying storage environment.

3.2 REAGENTS

The major reagent in this Research work is Urea. Other reagents include water, and oxygen of the air. For the purpose of this work, one bag of a 50kg urea fertilizer was bought. Oxygen is supplied using a car tire tube to which air is pumped to fill a rubber tube with a rubber clip to control the rate of oxygen (air) supply. Water is used to dissolve the urea, so that the quantity of water needed to dissolve a given quantity of urea is normally weighed with a sensitive measuring mass balance.

3.3 PROCEDURE

In carrying out the experimental work in this project, a preliminary test run of apparatus was conducted. In the course of this test-running, some quantity of urea were dissolved with water and through the separating funnel, the solution was put into the round bottom flask.

Then the heating mantle was connected to electricity and with a thermometer in position, the apparatus was switched on.

Gas was observed to evolve which when moistened red litmus paper was put in to the outcoming gas was turned blue

indicating that the gas coming out was an alkaline gas known as ammonia. The thermometer reading in the round bottom flask was observed to rise from room temperature of 27°C until it reaches 90-100°C when the urea solution starts boiling.

Before urea solution reaches a boiling point, the mercury manometer was observed to show no change in levels of the two arms. But once the boiling point is reached, bubble of water was observed to rise up to the delivery tube and consequently the mercury manometer was observed to show difference in rise.

At the reduction chamber the ammonia gas reacts with oxygen of the air from the car tire tube and is reduced to Nitrogen and water in form of steam. When both the Nitrogen and steam passes through the condenser the steam condenses while the Nitrogen passes into the second car tire tube where it is collected until when needed to be used in modifying the storage environment.

The preliminary test run experiment helped in knowing the parameters that need be controlled. From observation, it was noticed that the urea solution should not be allowed to reach boiling point as this causes the steam from urea solution to rise into the delivery tube and consequently

after the pressure as changes observed in the mercury in glass manometer. Again the steam if allowed enters the reduction chamber and then disturbs the reaction between ammonia and oxygen.

Therefore, there is need to control the experiment by not allowing the heating to reach 100°C . Once the thermometer in the round bottom flask reaches 90°C the heating mantle is switched off.

After the preliminary test run of the apparatus was carried out, then measurement of the components of the apparatus were carried out, using mass sensitive balance instrument.

Then some quantity of urea were measured and some water added to make a solution which were then run into the round bottom flask through the separating funnel.

In the reduction chamber, oxygen from the air is introduced from a car tire tube using a rubber clip and a connecting rubber. As the reaction progress, a red litmus paper placed at the mouth of the round bottom flask was observed to turn blue showing that ammonia is liberated.

Then as heating continues more ammonia is released and the

reaction continues at the reduction chamber with oxygen to give out Nitrogen which passes through a condense. The condenser ensures that any trace of water in vapour form condenses and only Nitrogen enters the second tube or any storage system: When the experiment stops, the components are reweighed to know the mass of residue and mass of ammonia released.

Further experiment was carried out in which the Nitrogen generated were directed into a maize container. This was done to know whether the nitrogen generated will help store the maize for sometime. Three maize containers were provided into one of the maize container, dry maize was stored and oxygen added.

Then into the second one maize was stored in the wet form and then nitrogen was also introduced. The last one served as control whereby no nitrogen was introduced. The three containers were kept for sometime before they were subjected to germination test.

CHAPTER FOUR

The following is the test description and measured physical properties.

TEST date: 22 - 02 - 2000

Reactants: Urea, Water, and Air

Weight of round bottom flask empty = 300g

Weight of Ammonia reduction chamber = 250g

Weight of empty tube (1) = 313g

Weight of empty tube (2) = 617g

Table 2: Weights of Urea, Water and Oxygen

Vs Volume of Nitrogen and Ammonia liberated

	Mass of urea (g) $\text{CO}(\text{NH}_2)_2$	Mass of water(g) H_2O	Volume of oxygen used (g) O_2	Vol. of Nitrogen(g) N_2	Volume of Ammonia lib- erated NH_3
	60	36	48	28	34
	70	42	56	33	40
	80	48	64	37	45
	90	54	72	42	51
	100	60	80	47	57
	110	66	88	51	62
	120	72	96	56	68
	130	78	104	61	74
	140	84	112	65	79
	150	90	120	70	85
Mean	105	63	84	49	59.5
Variance	30.28	18.17	24.22	14.09	17.12
C.V (%)	28.84	28.84	28.83	28.76	28.77

Table 2 above shows the relative weights of urea, water and Oxygen (air) used in the experiment and their corresponding Nitrogen and Ammonia released.

The coefficient of variation was obtained to be approximately 28.8% when corrected to one place of decimal which indicates the homogeneity of the experiment. Whereas there are variations in the means and variance of urea, water, air, Nitrogen and Ammonia, the coefficient of variation remain nearby the same as shown in the table. This table helps to show that the urea, the more Nitrogen will be generated.

Table 3: Ammonia yield at treatments with different rate of urea

Test date: 23 - 02 - 2000

UREA LEVEL (g)	REPLICATION				
	1	2	3	4	5
60	34.5	34.0	35.0	33.5	33.0
80	45.0	44.5	44.0	45.5	46.0
100	57.5	57.0	58.0	56.5	56.0
120	68.0	68.5	67.0	67.0	69.0
140	79.5	79.0	80.0	78.5	78.0
MEAN	56.90	56.70	56.90	56.2	56.4
VARIANCE	17.8e	18.08	17.98	17.63	17.90
CV(%)	31.41	31.89	31.60	31.38	31.73

Table 3 shows a situation where ammonia yield at treatment with different rates of urea is replicated. The means here are within 56 - 57 g and the coefficient of variation is within 31 - 32% when subjected for further statistical analysis the result shows a highly significant difference and find out that the means are statically the same.

Table 4: Nitrogen yield at treatment with different rates of urea

Test date: 24 - 02 - 2000

UREA LEVEL (g)	REPLICATION				
	1	2	3	4	5
60	28.0	28.5	27.5	27.0	29.0
80	37.0	37.5	36.5	36.0	38.0
100	47.0	47.5	46.5	46.0	48.0
120	56.0	56.5	55.5	55.0	57.0
140	65.0	65.5	64.5	64.0	66.0
MEAN	43.6	47.1	46.1	45.6	47.6
VARIANCE	14.71	14.71	14.71	14.71	14.71
CV(%)	31.57	31.23	31.90	32.26	30.90

In the table 4, Nitrogen yield at treatment with different rates of urea was shown. The situation was shown in a replicated form. A similar result to that of ammonia was obtained with coefficient of variation between 31 - 32% variance = 15.

Table 5: Air used with treatment at different rates of urea

Test date: 25 - 02 - 2000

UREA LEVEL (g)	REPLICATION				
	1	2	3	4	5
60	48.5	48.0	47.0	47.5	49.0
80	64.0	64.5	65.0	63.5	63.0
100	80.5	80.0	79.5	79.0	81.0
120	96.0	96.0	95.5	97.0	95.0
140	112.5	112.0	111.5	111.0	113.0
MEAN	80.3	80.2	79.10	79.6	80.2
VARIANCE	25.30	25.30	25.23	25.39	25.32
CV(%)	31.51	31.55	31.66	31.90	31.57

From table 5 air used with treatment at different rates of urea was observed to give a similar co-efficient of variation result as is found to be within 31 - 32% with almost constant variance at 25.

Table 6: Water used at treatment with different rates of urea

Test date: 26 - 03 - 2000

UREA LEVEL (g)	REPLICATION				
	1	2	3	4	5
60	35.6	36.0	37.0	35.5	35.0
80	48.0	48.5	49.0	47.5	47.0
100	60.5	60.0	61.0	59.5	59.0
120	72.0	71.0	71.5	72.5	73.0
140	84.5	84.0	85.0	83.5	83.0
MEAN	60.3	59.9	60.7	59.7	59.4
VARIANCE	18.98	18.74	18.75	19.14	19.37
CV(%)	31.47	31.29	30.88	32.05	32.51

Table 6 shows the water at treatment with different rates of urea. The variance was found to be almost constant at approximately 19, coefficient of variation lies between approximation of 31 and 32 %

Table 7: Nitrogen yield from urea subjected to simple regression

S/N	Yield of Nitrogen (N2) (CM3)		Urea used (g)				
	Y	X	X	Y	X ²	Y ²	XY
1	28	60	-40	-18.6	1600	345.96	744
2	37	80	-20	-9.6	400	92.16	192
3	47	100	0	0.4	0	0.16	0
4	56	120	20	9.4	400	88.36	188
5	65	140	40	18.4	1600	338.56	736
Sum:	233	500	0	0	400	865.2	1860
Mean	46.6	100					

$$b = \frac{\sum XY}{\sum X^2} = \frac{1860}{4000} = 0.465$$

In a simple regression equation

$$a = \bar{Y} - b\bar{X}$$

$$= 46.6 - 0.465 \times 100$$

$$a = 46.6 - 46.5$$

$$= 0.1$$

Predication equation now becomes

$$Y = 0.1 + 0.465 x$$

Where $b = \text{slope} = 0.465$

$a = \text{Intercept} = 0.1$

Table 8: Water and urea subjected to regression analysis

	Y	X	X	Y	X ²	Y ²	XY
	36	60	-40	-24	1600	574	960
	48	80	-20	-12	400	144	240
	60	100	0	0	0	0	0
	72	120	20	12	400	144	240
	88	140	40	24	1600	574	960
	-----	-----	-----	-----	-----	-----	-----
Sum:	300	500			4000	1440	2400
Mean	60	100					

$$b = \frac{\sum XY}{\sum X^2} = \frac{2400}{4000} = 0.6$$

$$\begin{aligned} a &= \bar{Y} - b\bar{X} \\ &= 60 - 0.6 \times 100 \\ &= 60 - 60 = 0 \end{aligned}$$

Slope = 0.6

Intercept = 0

For each unit change in urea used there is a corresponding unit increase of 0.6 cm³ of water used that is associated with urea.

The regression coefficient

$$R^2 = \frac{bExy}{Ey^2} = \frac{0.6 \times 2400}{1440} \\ = 1$$

The prediction equation can now be interpreted as: for each unit change in x (the urea used) there is a corresponding yield in y (the nitrogen generated) of 0.465 starting at yield of y = 0.1 and the regression co-efficient given by:

$$R^2 = \frac{bExy}{Ey^2} = \frac{0.465 \times 1860}{865.2} \\ = 0.9997 = 99.97\%$$

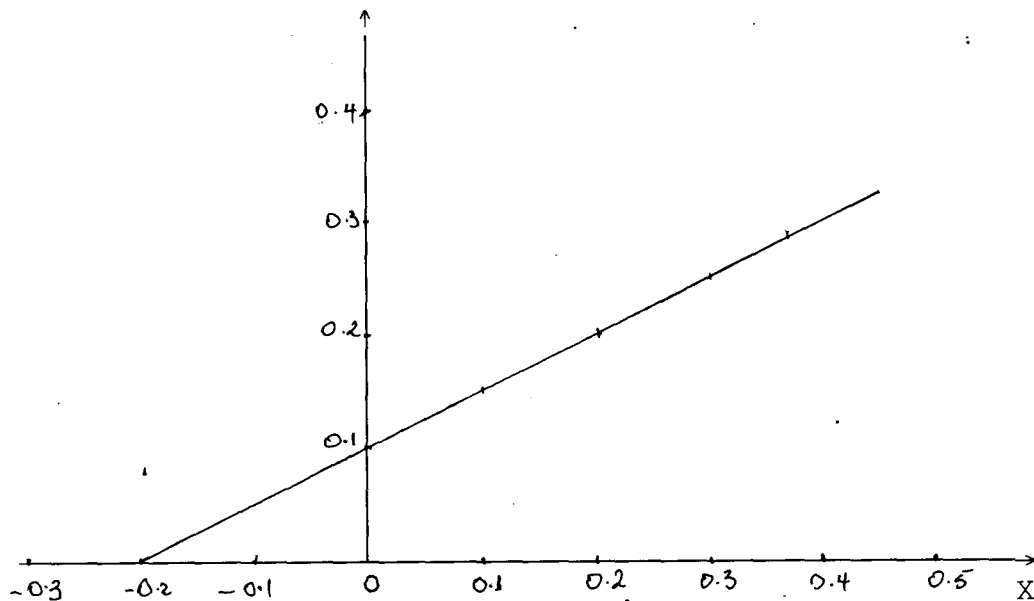


Fig 5: Graph of Nitrogen yield Vs Urea used.

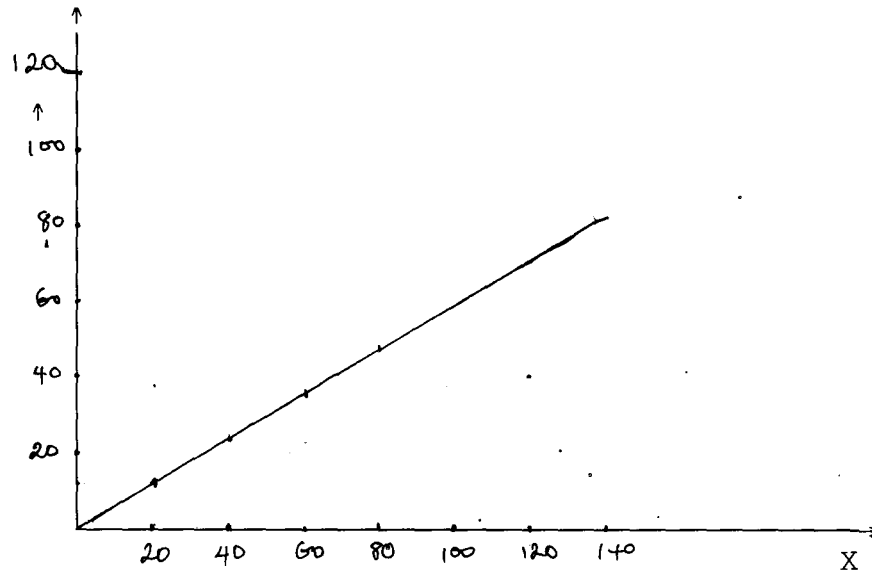


Fig 6: Graph of urea vs water used in the experiment

Table 9: Urea Vs Oxygen used in reaction subjected to regression analysis

	Y	X	X	Y	X ²	Y ²	XY
	48	60	-40	-32	1600	1024	1280
	64	80	-20	-16	400	256	320
	80	100	0	0	0	0	0
	96	120	20	16	400	256	320
	112	140	40	32	1600	1024	1280
Sum:	400	500			4000	2560	3200
Mean	80	100					

$$b = \frac{\sum XY}{\sum X^2} = \frac{3200}{4000} = \frac{4}{5} = 0.80$$

$$\begin{aligned}
 a &= \bar{Y} - b\bar{x} \\
 &= 80 - 0.80 \times 100 \\
 &= 80 - 80 = 0 \text{ no intercept}
 \end{aligned}$$

Prediction equation $Y = 0.8 x$

For each unit change in urea used there is a corresponding change in Oxygen used of 0.8cm^3 starting from origin.

Regression co-efficient

$$R^2 = \frac{bE_{xy}}{E_y^2} = \frac{0.8 \times 3200}{2560} = 1$$

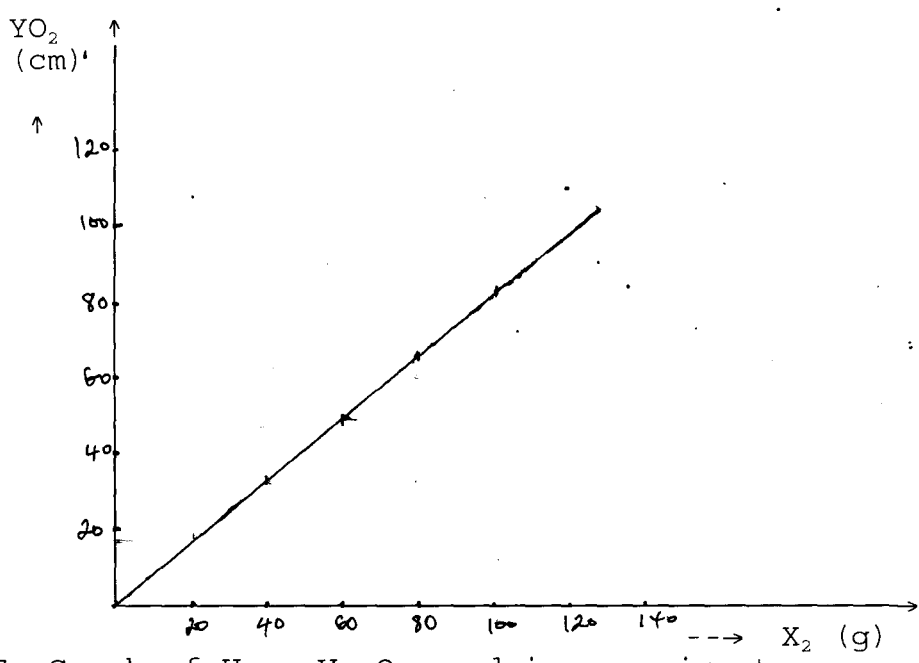


Fig 7: Graph of Urea Vs O_2 used in experiment.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

From the experimental results we can observed that the quantity of urea used determined the quantity of water to be used to dissolve it, and the quantity of Nitrogen generated.

This implies that the more urea used is dissolved with more quantity of water and the more Nitrogen is generated.

In view of the fact that this pilot experimental project on generation on Nitrogen from urea for modifying storage environment has been carried out by the author in partial fulfillment for the award of bachelor of technology degree programme, considering the fact that their project was unaided and hence the author has single handedly tried to project the use of the urea in generating Nitrogen which is known to play an active part in inert atmospheric storage. This project can not be termed a colossal failure in that there was an evident observation that ammonia was generated as soon as urea solution was heated up; by ammonia's irritating smell and its ability to turn red litmus paper

blue.

5.2 RECOMMENDATION

The author experienced the problem of raising the temperature of the second reaction chamber where ammonia has to react with oxygen to give nitrogen.

According to text book recommendation this temperature under industrial set-up has to reach 500^oc of which in this pilot study the design was not to achieve this temperature of 500^oc. Hence the yield of Nitrogen was found not to be appreciable.

In the light of the work done and the above explanation, I hereby plead with the authorities concerned to give a consideration to effort made so far by the author.

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