POWDERED OR GRANULAR DAP:

THE USE OF FLORIDA ACID IN A PIPE REACTOR

For Presentation at the AIChE

Joint Meeting

Clearwater, Florida

May 24, 1986

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INTRODUCTION

The manufacture of ammonium phosphates is carried out by neutralizing phosphoric acid with ammonia. The reactions involved:

$$NH_3 + H_3PO_4 \longrightarrow NH_4H_2PO_4 \text{ (MAP)}$$

$$NH_3 + NH_4H_2PO_4 \longrightarrow (NH_4)_2HPO_4 \text{ (DAP)}$$

are exothermic and the heat of reaction is used to evaporate water from the phosphoric acid solution.

The ERT-ESPINDESA process for the manufacture of ammonium phosphates, either powdered or granular, is based on the use of a special reactor of propietary design which achieves the reaction of ammonia and phosphoric acid up to NH_3/H_3PO_4 molar ratios above 2.0 in a single piece of equipment. Ammonia spillage from the reactor amounts to only 10-15% of the feed.

A melt of MAP or DAP mixed with water vapour is produced in the pipe reactor and therefore the manufacture of powdered or granular MAP or DAP is achieved by spraying the melt from the top of a tower or alternatively spraying it inside a rotary drum when granular product is to be produced. Florida acid has been tested with excellent results.

The development of the pipe reactor

Since 1966 the ERT fertilizer complex located at Huelva has been manufacturing powdered MAP, some of which is used in a neighboring NPK granulation plant. The rest is exported by train, truck or ship to other ERT plants in Spain.

POWDERED MAP VIA PIPE-REACTOR

The old ERT Minifos plant was retrofitted in 1981 with the pipe reactor to produce 450 Tpd of low moisture powdered MAP.

The process consists of a pipe reactor located at the top of a tower 17 meters high. The pipe reactor is made of stainless steel and is fed with phosphoric acid and ammonia to produce a melt of MAP which solidifies when falling inside the tower (Fig. 1).

The moisture of the product is controlled by adjusting the acid strength of the phosphoric acid fed to the pipe (see Fig. 2) in such a way that for a certain P_2O_5 content in the phosphoric acid and a molar ratio NH_3/H_3PO_4, a given moisture in the MAP is obtained. Usually the moisture of the product is kept at a level of 4-6% to have a free-flowing product. Lower moisture means dust losses, and higher moisture could cake the product and make transport more expensive. Another factor influencing the caking tendency is the acidity of the product. Low pH increases the chances of caking.

The tower is natural-draft type. The product is collected in the bottom as a powder, at a temperature of 60ºC. It can be stored without caking or directly used as an intermediate in the manufacture of NPK granules.

Ammonia losses are almost negligible and therefore the cooling air from the tower can be scrubbed with phosphoric acid or water, to recover the entrained MAP particles. If phosphoric acid is used as a scrubbing liquor, the acid is used as feed to the pipe reactor. In the case of using water, a part of the water is used to dilute the feed acid.

Features of the system:

- Very simple plant design, i.e. low investment
- Easy operation
- Moisture of MAP can be adjusted from 2% to 12%
- Very high ammonia and P_2O_5 efficiencies
- Low energy consumption (3 kWh/t of MAP and 15 kg steam/t of MAP if vaporized ammonia is used or 130 kg in case of using liquid ammonia).
- When 44-45% P_2O_5 phosphoric acid is used as raw material, the MAP contains 4-5% moisture, which means a savings of steam in the concentration step of phosphoric acid equivalent to 100 kg of steam per each 1% of concentration.

THE LOW RECYCLE GRANULAR DAP PROCESS

In the ERT-ESPINDESA pipe reactor, ammonia and phosphoric acid are reacted under pressure, in a very short time, in such a way that almost all the heat of reaction is evolved inside the pipe. Consequently most of the water is evaporated from the phosphoric acid solution. This yields a much more concentrated DAP melt than would be obtained in a conventional reaction vessel, which means that lower quantities of material need to be recycled to the granulator. The need for pumping slurries close to their solidification point is also avoided. The ammonia to phosphoric acid molar ratio reaches 2.05:1.0 and there is no need to add further ammonia to the granulator.

When compared to the conventional DAP granulation processes, the ERT-ESPINDESA low-recycle process offers a number of advantages for the manufacture of DAP. The process has a low recycle ratio 2.5-3 (a conventional granulation process typically has a recycle ratio of 4-6). It is also easier to operate, for example: there is only one ammonia feed to the plant; fewer pieces of equipment are needed; no hot slurries are pumped; and there is no need for an ammonia sparger in the granulator. These features mean that operating costs are lower. The investment required for a new plant is also smaller because of the smaller equipment size (due to the lower recycle ratio) and the simpler lay-out that can be achieved.

The process has several other advantages: P_2O_5 in the product has a high solubility in water (98% compared with 90-92% for DAP produced in conventional processes with Morocco acid). Production rates in existing DAP plants can be increased by up to 50% by retrofitting the ERT-ESPINDESA pipe reactor. Acids with a high impurity content can be employed as feed-stock; several phosphoric acids containing significant amounts of gypsum and magnesium have been tested and the quality of the DAP produced was excellent. It is also possible, in the same plant to produce a wide range of NPK formulations.

Process description

An outline of the ERT-ESPINDESA low-recycle DAP process is shown in the Fig. 3. Initially, phosphoric acid with a concentration of 40% P_2O_5, or higher, is fed to a two-stage ammonia scrubber, where it absorbs most of the ammonia lost in the granulator. A pump is used to transfer the acid between the two sections of the scrubber. From the ammonia scrubber, the partially neutralized phosphoric acid, with an ammonia to phosphoric acid molar ratio of about 0.25, is pumped to the pipe reactor, where it reacts under pressure with ammonia to a final molar ratio of 1.9-2.05, depending on the impurities present in the acid feed. The reaction is instantaneous and exothermic, and part of the water content of the phosphoric acid evaporates to dissipate the heat of the reaction. NO AMMONIA IS ADDED DIRECTLY TO THE GRANULATOR. Excess ammonia is recovered in the ammonia scrubber, as described. The mixture of air and water vapor removed from the ammonia scrubber is passed through a final gas scrubber before it is discharged to the atmosphere.

From the pipe reactor, the hot concentrated DAP melt is sprayed over recycled DAP in the granulator, which is of the rotary drum type and lined with self-cleaning rubber panels. Due to the low water content of the hot DAP melt, the recycle ratio can be kept between 2.5 and 3.5. At the exit of the drum, the moisture content of the product is below 3.0%

Granulated product falls directly into a rotary drier where it is dried to the desired moisture content. Product leaving the drier is sent, via a bucket elevator, to the screens, where it is divided into three streams: oversize, product and the fines. The coarse fraction (oversize) is passed to the mill where the crushed material is discharged, together with the fines from the screen, into a storage bin. The output from this bin is regulated in such a way that a constant feed of material is recycled to the granulator. The on-size material from the screen is conveyed to storage.

Hot air from the drier is removed through cyclones to the same gas scrubber as the gases from the ammonia scrubber before being discharged to the atmosphere.

Raw materials and utilities consumptions for producing granular DAP (18-46-0)

Raw materials consumptions, t/t

Ammonia (100% NH_3)	0.221
Phosphoric acid (100%) P_2O_5)	0.463

Utilities consumptions

Steam, kg/t	1
Electricity, kWh/t	25
Fuel Oil, kg/t	2

Raw materials and product quality

Phosphoric acid feed analysis: (Acid from Morocco rock)

P_2O_5	40.15
F	1.41
SO_3	1.943
SiO_2	0.47
CaO	0.79
Al_2O_3	0.434
Fe_2O_3	0.457
MgO	0.439
Na_2O	0.164
K_2O	0.017
Cl^-	0.033
Org. Mat.	0.02
Susp. Solids	2.44

DAP Analysis obtained with that acid

N	18.25
Water soluble P_2O_5	45.12
Citrate soluble P_2O_5	46.44
Total P_2O_5	46.57

$$\frac{\text{Water sol. } P_2O_5}{\text{Total}} = 96.886\%$$

$$\frac{\text{Citrate sol. } P_2O_5}{\text{Total}} = 99.72\%$$

Attention should be brought to the high water and citrate solubility of P_2O_5 of the DAP produced with this process. No further studies have been done to explain this fact but it seems possible that the short residence time of reactants inside the reactor do not allow P_2O_5 to form some of the non-soluble salts which usually appear when making commercial grade DAP.

Pipe reactor description

Depending on the phosphoric acid impurities, the pipe-reactor can be made of 316 L SS or Uranus 36. Some of the reactors used at ERT's Huelva works are now in the third year of operation.

Pipe diameter and length are variable according to the design rate. For 25 t/h of DAP the diameter is 4 inches and the length is 20 feet. Only 5 feet are placed inside the granulator.

The pipe-reactor is supported outside the granulator and therefore the retrofitting of an existing granulator is very simple.

POWDERED DAP

In view of the fact that ammonia spillage from the pipe reactor was on the order of 10-15% of the feed when the ammoniation of phosphoric acid was conducted at molar ratios NH_3/H_3PO_4 close to 2.0, the idea was developed of producing DAP in a different form: powdered.

On the other hand some of the NPK formulations low in nitrogen (i.e. 8-24-8, 5-15-15, etc.) do not admit only DAP as a source of nitrogen and P_2O_5. We came to the conclusion that the ideal situation would be to have a plant able to produce any ammonium phosphate with a molar ratio NH_3/H_3PO_4 between 1.0 and 2.0.

The benefits of fixing double amount of ammonia (the cheapest source of nitrogen) to the phosphoric acid and making a product that could be used as ingredient in granulation and fluid fertilizer plants, were clear. In the ERT plants in Spain alone the savings amounted to several million dollars.

In other words, we tried to combine the advantages of powdered MAP and the chemical composition of DAP.

Pilot plant

A pilot plant was erected consisting of a forced-draft tower provided with a pipe reactor of a capacity of 400 kg/h DAP in a similar way to Fig. 1.

The first trials were conducted with Morocco acid.

After the necessary adjustments, a free flowing powder of DAP was obtained. Moisture of the product was on the order of 6-10% and could be easily varied by adjusting the acid strength of the feed. The solubility of the product was 97-98%.

By adjusting the acid strength, both the molar ratio and the moisture of the product can be optimized.

The performance of the pilot plant pipe reactor is identical when producing powdered or granular DAP. The operating conditions are the same.

The heat of reaction of the phosphoric acid made from Moroccan rock varies between 1300 and 1500 kcal/kg of ammonia, depending on the impurities of the acid.

Senegal acid has also been tested and has given excellent results, quite similar to the Moroccan acid, except for some foaming tendency, which required the addition of antifoaming agents.

Florida acid tests

Two different types of acid were used to test the plugging tendency performance of the pipe-reactor with acids of different solids content and reactivity. Table I gives the analysis of the acids. Type B is sludge acid (bottoms of a Lamella thickener)

TABLE I

	Type "A"	Type "B"
P_2O_5	47.03	42.64
CaO	0.33	0.60
SiO_2	0.11	0.11
Fe_2O_3	2.43	3.85
Al_2O_3	1.73	1.84
F	1.45	1.55
H_2SO_4	4.80	5.50
Na_2O	0.17	0.17
K_2O	0.14	0.36
MgO	0.73	0.73
Solids (methanol)	6.50	16.40

Some de-foamer was added (not necessary with Moroccan acid) and the following typical analysis of the product were obtained (dry-basis):

Nitrogen	17.15-17.93%
P_2O_5 water sol	41.68-44.47%
P_2O_5 citrate sol	46.16-49.00%
P_2O_5 total	46.21-49.03%
pH	7.39-7.27

Some short trials were done to raise the ammoniation of the acid and in one case the pH of the product rose up to 8.3 which is well above DAP, but as the aim of the tests was mainly to demonstrate that neither plugging nor scaling appeared, no effort was devoted to the optimization of the process conditions to produce DAP with the above acids.

No attempt to produce DAP was done with sludge acid. Only MAP was tried in the same pipe reactor. The results were the following:

Nitrogen	9.78%
P_2O_5 water sol	41.53%
P_2O_5 citrate sol	50.75%
P_2O_5 total	50.78%
H_2O (Karl-Fisher)	1.94%
pH	4.1

No plugging of the pipe-reactor was experienced with any of the acids.

Retrofitting of a powdered MAP plant to powdered DAP

At the time of preparing this paper, the existing 450 t/d MAP tower in Huelva is being retrofitted to the manufacture powdered DAP.

The retrofitting of the plant is so simple that the estimated pay-out time of the retrofit is less than 4 months.

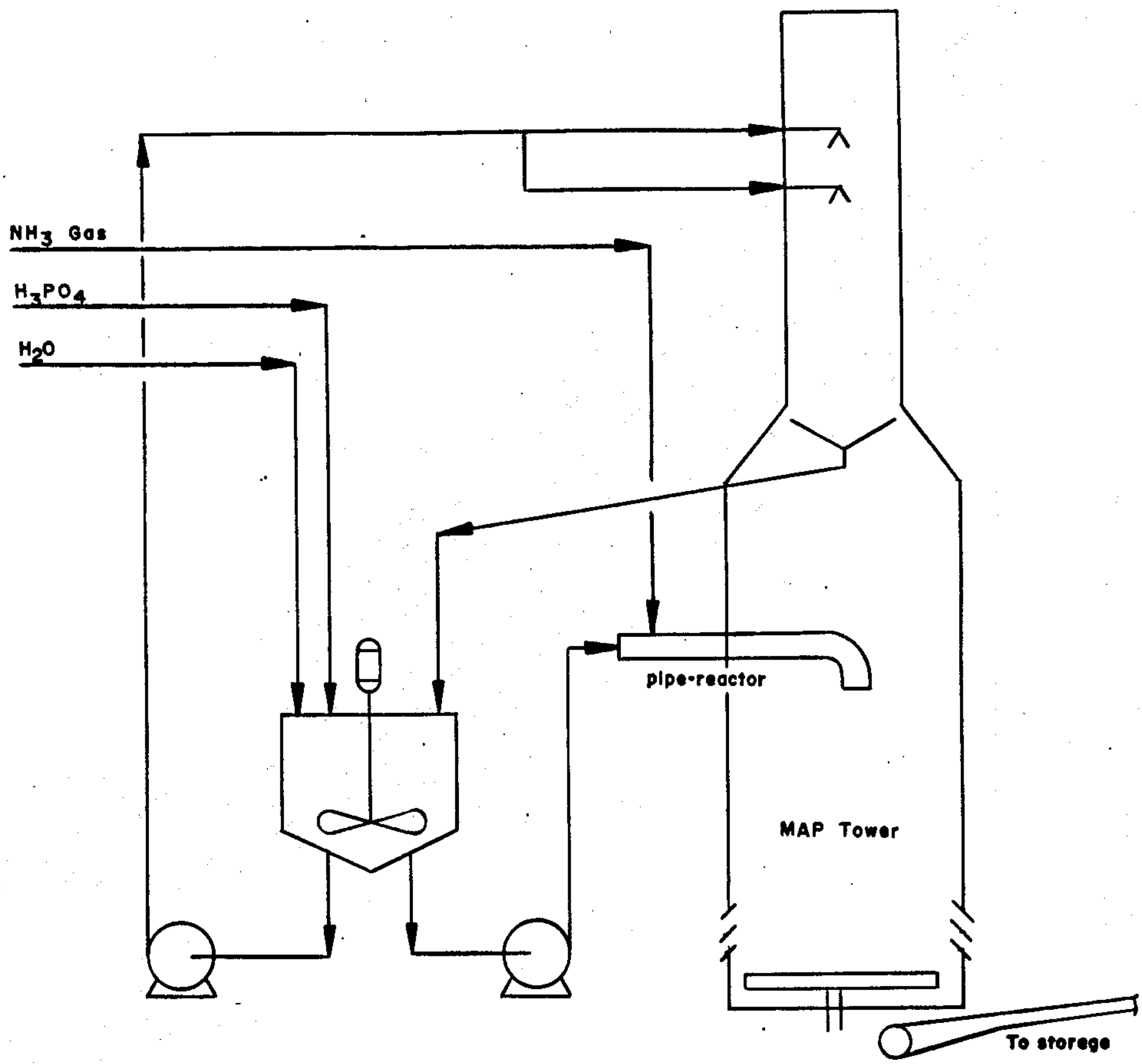

FIG. 1

ERT – ESPINDESA Process for MAP

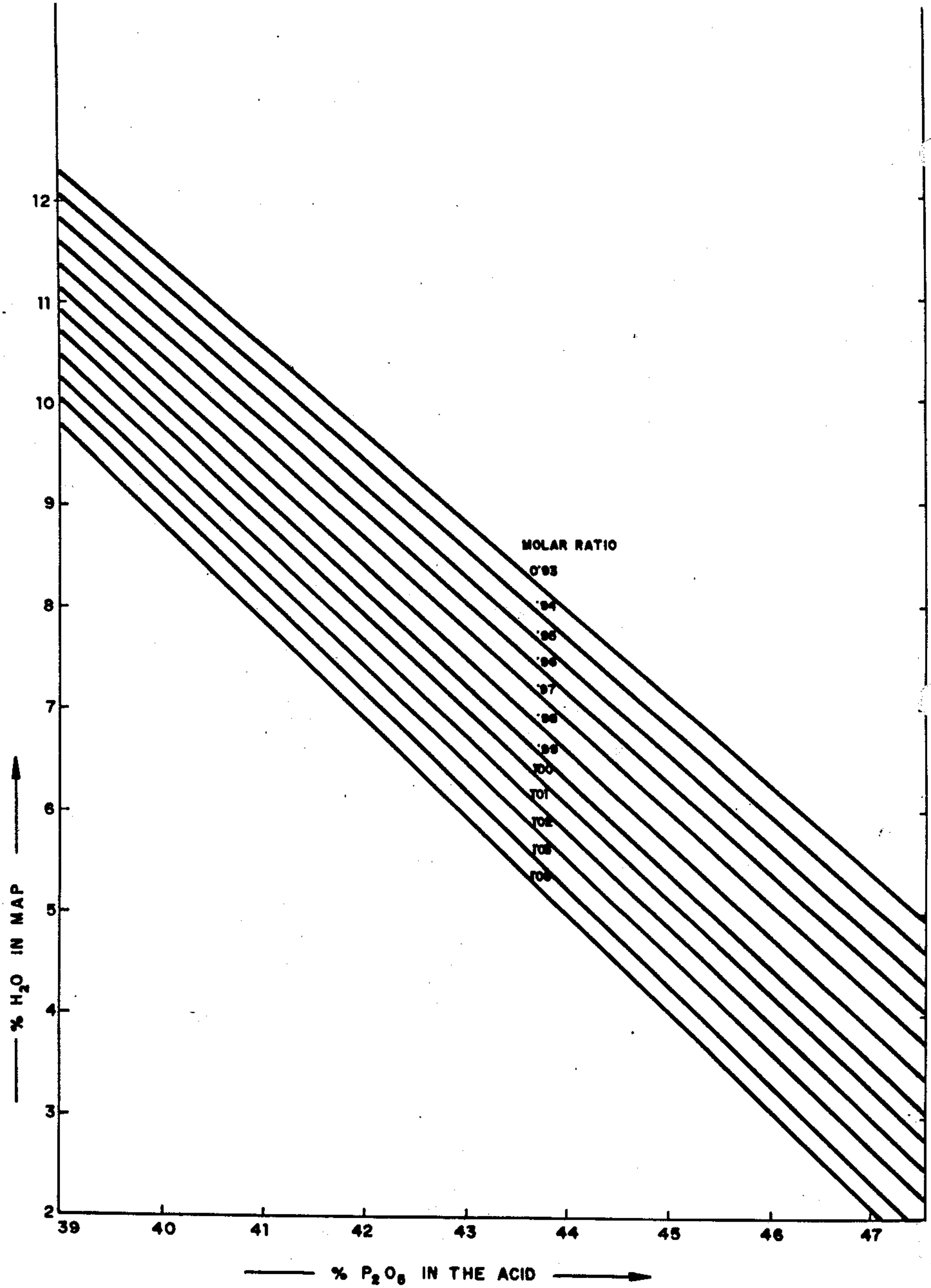

Fig. 2.- MOISTURE OF THE MAP VS P_2O_5 CONTENT OF THE ACID FEED.

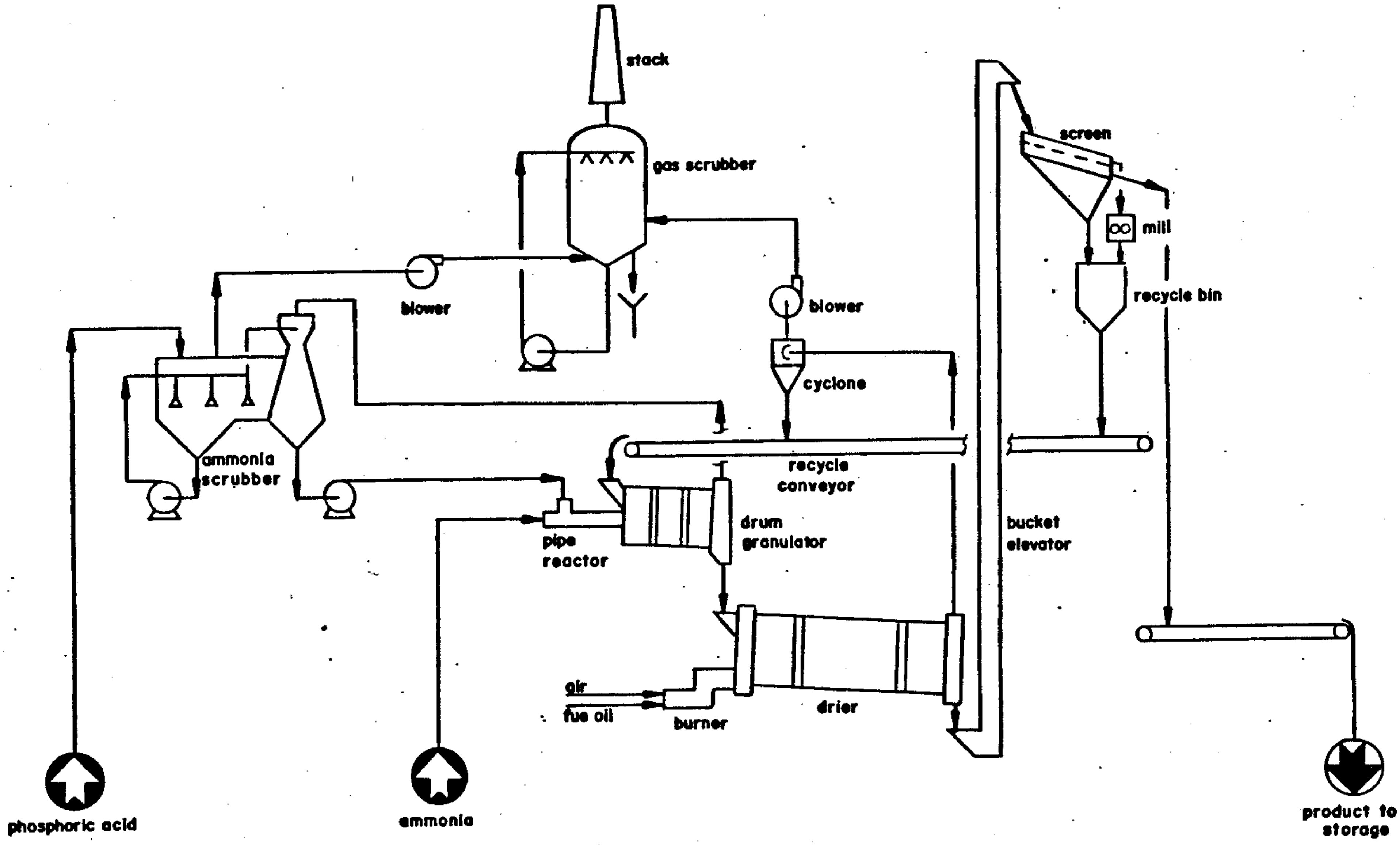

Fig. 3

The ERT-ESPINDESA Low Recycle DAP Process.