

DEVELOPMENTS IN THE APPLICATION OF THE ACID PRE-CLARIFICATION (A.P.C.) PROCESS TO PRACTICE

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The following points cover developments whereby the difficulties in the filtration of the first precipitate or slurry can be overcome. The treatment of the resulting filter cake from a cane wax angle and the use of the wax-free residue as a fertilizer filler are discussed. Comparative figures using the Oliver-Campbell cake by existing methods have been made.

The Acid Pre-Clarification Process

Initial pH.

The fixing of the pH point at 3.2 is unnecessary in practice provided the figure is 3.2 or lower. At lower pH values more sulphur is used, but this is offset by more rapid precipitation, smaller slurry volume and better and quicker settlement of the final clarified juice. Thus:—

| pH | Per cent. SO ₂ | Tons Sulphur per 3,000 tons cane |
|-----|---------------------------|----------------------------------|
| 3.2 | .057 | .85 |
| 2.8 | .076 | 1.14 |
| 2.4 | .106 | 1.59 |

This latitude means that a sulphur tower can be used, thereby doing away with the major difficulties in the production and use of liquid or aqueous sulphur dioxide.

The Acid Pre-Clarification Process in Practice

To the mixed juice a pre-determined quantity of phosphoric paste is added depending on the quality of sugar to be made. 0.3 gms per litre of juice is a normal figure but good clarity can be obtained without any additional P₂O₅.

The cold juice is then passed through a sulphur tower of efficient design and immediately led, preferably by gravity, into special subsiders (Fig. 2) made of wood, or acid-resistant material. The anti-acid paint produced in Johannesburg is worth an extended trial.

The vats should be provided with baffles to minimise vibration effects on the floc, and a slow stirring device so as to reduce the volume of the precipitate to a minimum. On the other hand should part or all of the slurry pass by accident over into the supernatant liquid, no harm would occur, as it will all be limed, giving one final precipitate instead of two.

Time of settlement has only the effect of increasing capacity requirements, as there is no inversion or

fermentation over extended periods at atmospheric temperature. The reason for this is that sulphurous acid is too weak an acid to cause inversion at normal temperature and its germicidal properties act as an inhibitor of fermentation.

The supernatant liquid, 90 per cent. of the total volume, is limed to 8 pH, heated and settled in Bach subsiders. This mud can be easily filtered in any type of filter.

Filtration of the Slurry

Filtration of the slurry depends on the established fact that if the acid slurry is limed to 8 pH, heated, mixed with bagacillo and filtered on an Oliver-Campbell filter in the normal manner, the resulting cake can be heavily diluted, the bagacillo removed over a 10-mesh vibrating screen and the effluent boiled to 15 minutes, with or without the addition of 0.3 per cent. sulphuric acid. It is then resettled and the light mud filtered through a plate and frame press, which filters it readily.

To avoid this complicated treatment the original mud after liming to 8 pH is heated and pressed, thereby eliminating the Oliver-Campbell filter.

For wax recovery the cake should have an initial moisture content of less than 65 per cent., when it can be extruded through a noodle machine. In this form the cake can be easily dried and efficiently extracted in a short time. If sulphuric acid is used, the wax content of the dried noodles will range from 30 to 40 per cent. Without the use of acid the wax content will be approximately 5 to 6 per cent. lower.

Comparative Figures using Sulpho-Defecation and Acid Pre-Clarification Oliver-Campbell Filter Cake

Normal Oliver-Campbell filter cake can be treated in the same way. Thus samples of cake averaging 73.7 per cent. moisture and 26.3 per cent. dry solids including the added bagacillo, were washed with five successive lots of water over a 10-mesh screen. This coarse screen is advisable so as to allow some of the fine bagacillo to pass and assist in the final filtration. The coarse bagacillo is successively squeezed by hand to remove the excess liquid.

The extraction of precipitated solids is shown in the following averages on 100 gms. samples of Oliver-Campbell cake containing 16.4 gms. dry filtered solids.

| | | | | |
|------------------------|------|-------|-------|-------|
| Ccs. wash water ... | 250 | 100 | 100 | 100 |
| Av. gms. dry solids . | 7.12 | 10.02 | 11.67 | 12.26 |
| Per cent. extraction . | 43.5 | 61.2 | 71.3 | 74.9 |

In practice the Oliver-Campbell cake is diluted, stirred and sieved and the effluent boiled and settled. Under comparative laboratory conditions the average results were:—

| | | | | |
|-------------------|-----|-----|-----|----------------|
| Dried bagacillo . | ... | ... | ... | 33.8 per cent. |
| Dried filter cake | ... | ... | ... | 49.6 per cent. |
| Solids lost . | ... | ... | ... | 16.6 per cent. |

100.0

Basing these figures on 1,000 tons of cane, then there are 56 tons of Oliver-Campbell cake containing 14.7 tons of dry material, of which 4.97 tons is bagacillo. On treatment, 7.29 tons precipitated solids are recovered and 2.4 tons lost in the effluent.

On a weekly crush of 20,000 tons of cane there are 1,120 tons of wet Oliver-Campbell cake, containing 294 tons of dry material of which 146 tons can be

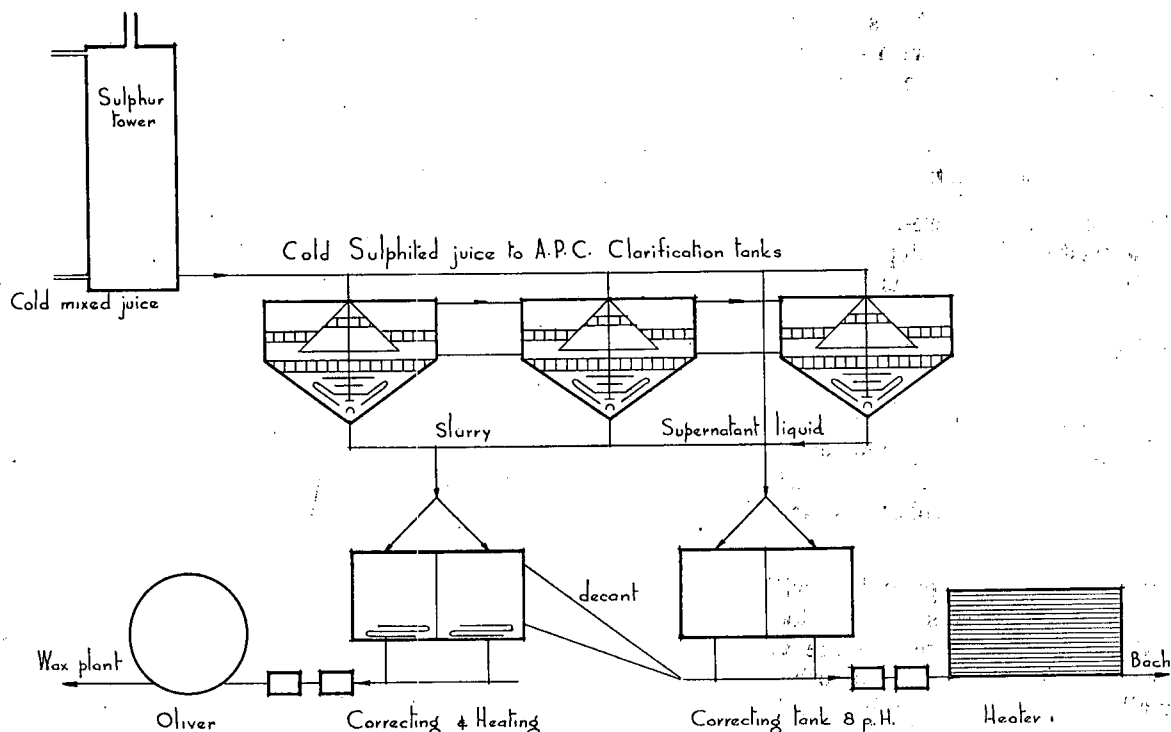
reprecipitated and filtered. This material is produced as previously described, in the form of worms or noodles. In this form it can be previously enriched with any desired quantities of N.P.K. so that instead of carting 1,120 tons of wet Oliver-Campbell cake to the fields, only 146 tons of the dry precipitate in convenient form, become available.

The sieved-out bagacillo is either discarded, briquetted for drying and burning, or returned and re-used on the Oliver-Campbell filters.

Comparisons with the Acid Pre-Clarification Process

The comparative amount of neutralised dry solids resulting from the acid pre-clarification process can vary from 116 to 160 tons per week depending on the dilution used. The increase in such solids by liming the slurry to 8 pH, is shown in the following figures:

| | Gms. acid solids | Gms. solids at 8 pH |
|-------------------------------|------------------|---------------------|
| 5 litre samples mixed juice, | | |
| diluted 4 : 1 | 24.94 | 29.78 |
| Tons per 20,000 tons cane ... | 98.40 | 117.60 |



(Fig. 1)

Other Comparisons: Cane Wax

On the basic figures of 146 tons of dry precipitate from normal filter cake and 118 tons from the acid pre-clarification process the following results were obtained:

| | Oliver Cake | Bagacillo | Filter Cake | Lost |
|---|----------------|-----------|----------------|------|
| Wax per cent. ... | 8.15 | 0.03 | 11.06 | — |
| Wt. of products per 1,000 tons of cane | 14.7 | 4.97 | 7.29 | 2.40 |
| Wt. wax tons ... | 1.20 | 0.02 | 0.81 | 0.37 |
| Per cent. recoverable | — | 1.60 | 67.5 | 30.9 |

On 20,000 tons of cane there would be 24 tons of wax in the filter cake, of which only 16 tons would be recoverable in the precipitated solids.

In the acid pre-clarification process the results were:

| | Gms. acid solids | Gms. solids at 8 pH |
|---|---------------------|------------------------|
| Weight of dry product from 20,000 tons of cane ... | 98.40 | 117.60 |
| Wax per cent. ... | 36.96 | 30.86 |
| Tons recoverable ... | 36.36 | 36.29 |

On 20,000 tons of cane, normal Oliver-Campbell cake therefore retains 24 tons of cane wax, whereas the acid pre-clarification process precipitates 36 tons in the slurry on first precipitate alone. Numerous figures confirm this large but variable difference in wax retention by the two processes. To which extent this loss is due to emulsification and loss of the fatty substances in the cane wax complex, has not as yet been determined, but it is of importance in sugar fabrication.

Other Comparisons: Nitrogen

On the comparative basis as above, a protein balance shows the following results:—

| | Oliver Cake | Bagacillo | Filter Cake | Lost |
|---|----------------|-----------|----------------|------|
| Nitrogen per cent. ... | 1.26 | 0.77 | 1.68 | — |
| Protein ... | 7.87 | 4.81 | 10.50 | 2.40 |
| Tons products per 1,000 tons of cane | 14.7 | 4.97 | 7.29 | 0.15 |
| Tons protein ... | 1.15 | 0.24 | 0.76 | 0.15 |

By the acid pre-clarification process the neutralised solids contained 2.66 per cent. nitrogen or 16.62 per cent. protein, so that on a 20,000 ton basis the comparative tonnages of protein are:—

| | Filter cake | Precipitated filter cake | A.P.C. slurry |
|-------------------|----------------|-----------------------------|------------------|
| Wt. protein, tons | 23.1 | 15.3 | 19.6 |

The Oliver-Campbell cake is the highest on account of its additional bagacillo content. The acid pre-clarification solids show 4.3 tons more protein removed than in the normal Oliver-Campbell cake. Maximum and minimum protein contents of acid pre-clarification slurry have been found to vary from 12.5 to 21.5 per cent.

Ash

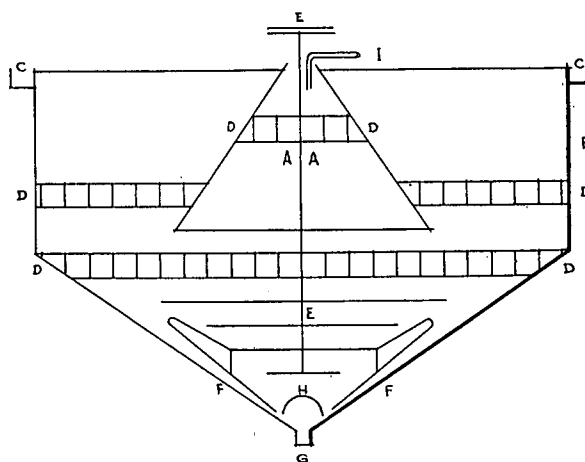
The comparative ash contents of these two products are as follows:—

| | Oliver Cake | Bagacillo | Filter Cake | Lost |
|---|----------------|-----------|----------------|------|
| Ash per cent. ... | 27.83 | 9.66 | 43.84 | — |
| Tons products per 1,000 tons of cane | 14.7 | 4.97 | 7.29 | 2.40 |
| Tons ash ... | 4.09 | 0.48 | 3.20 | 0.41 |
| Tons ash recovered... | 100.0 | 11.7 | 78.2 | 10.1 |

The washing and reprecipitation process therefore removes 10.1 per cent. of ash in the effluent and 11.7 per cent. in the bagacillo.

The neutralised acid pre-clarification slurry contains 23.34 per cent. ash so that on 20,000 tons of cane there are:—

| | Sulpho- Defecation | A.P.C. Process |
|------------------|-----------------------|-------------------|
| Tons product... | 146.0 | 118.00 |
| Ash per cent.... | 43.84 | 23.34 |
| Tons ash... | 63.90 | 15.70 |



(Fig. 2)

- A. Cone angle 45°. Acid resistant material.
- B. Pre-Clarification tank.
- C. Launder for supernatant liquid.
- D. Baffles.
- E. Slow moving thickening gear.
- F. Scraper to outlet G.
- G. Thick slurry.
- H. Cone with small hole to prevent channeling.
- I. Inlet cold mixed juice, 3.2 pH or lower.

This large difference is due to the smaller amounts of chemicals used in the acid pre-clarification process.

The silica content is 13.4 and 52.2 per cent. respectively, representing 8.56 and 8.20 tons entrained. Much of the iron is removed by washing and reprecipitation as, for example, the acid slurry normally contains 11 per cent. of iron in the ash. After dilution and reprecipitation this is almost totally removed, leaving an ash containing 99 per cent. SiO_2

Summary

On a total crop of 600,000 tons of cane there are in the products described, the following amounts:—

| | Tons dry cake | Tons wax | Tons protein | Tons ash |
|---------------------------|------------------|-------------|-----------------|-------------|
| Sulpho-defecation ... | 4380 | 720 | 459 | 1917 |
| A.P.C. neutralised Slurry | 3540 | 1080 | 588 | 471 |

Preparation of the Cake

The drying of filter cake has been solved by extruding it in the form of nodules. Normally a crop of 600,000 tons will produce 33,600 tons of wet Oliver-Campbell cake. By washing and filtering, drying and extracting, 8,820 tons of dry material are obtained—a saving in cartage of 24,780 tons of water and bagacillo.

This may be enriched with any quantities of N.P.K. By incorporating super-phosphate, the phosphate would be enveloped in the organic matrix and therefore have less chance of becoming fixed in the soil.

Advantages of the Acid Pre-Clarification Process from a Sugar Angle

The foregoing data supplement the information contained in previous papers on this subject. The point has now been reached when only full scale trials can confirm this laboratory data.

The benefits claimed are:—reduction in the amounts of sulphur, lime and phosphoric used; reduction in total amount of filter cake produced, its more efficient handling, drying and extraction; better retention of wax and improved clarification with decreased fermentation losses over shut-downs.

Mr. Antonowitz was struck by the small quantity of ash left in the juice after the acid pre-clarification process. He thought that by removing the proteins, glucosates and lime were also removed. These played an important part in keeping the ash in

solution. From that point of view, therefore, he thought this process showed great advantages.

Mr. Farquhar mentioned that he had seen a process in India where the juice was heated to 140° and then sulphited down to 3 pH. Then some slight precipitation was allowed in the Bach clarifier and the juice was then boiled in open tanks. They obtained a very good recovery and an excellent quality of white sugar for India.

Mr. Dymond pointed out that this process varied from the acid pre-clarification process in that the juice was heated and no attempt was made to separate the two precipitates.

Dr. Douwes Dekker enquired why a special type of clarifier had to be used rather than the ordinary Dorr or Bach clarifier.

He also said that, according to the average wax content of 113 samples of first precipitate provided in 1951 by Mr. Dymond and analysed by the National Chemical Research Laboratory in Pretoria, the total weight of wax available for extraction in the first precipitate from 20,000 tons of cane averages 23.85 tons. Mr. Dymond had now stated that 36.36 tons were recoverable from first precipitate and Dr. Douwes Dekker would like to know why 52 per cent. more wax was now expected to be recoverable. From the figures given by Mr. Dymond of tests on the wax content of Oliver-Campbell cake it would appear that if the sulpho-defecation process is applied a considerable quantity of wax goes into process. This quantity can leave the factory either in final molasses or in sugar. Analyses carried out at the S.M.R.I. allow the estimation of this total quantity at 3.20 tons for 20,000 tons of cane, and on the basis of this result one would expect 25.26 tons of wax to be available for extraction in the Oliver cake. This agrees fairly well with the quantity of 24 tons mentioned by Mr. Dymond, which shows, if the quantity of wax precipitated in the secondary precipitate (4.61 tons) is properly taken into account, that the figure given by Mr. Dymond for tons of wax recoverable from first precipitate (36.36 tons) is much too high.

Dr. Douwes Dekker could not see why Mr. Dymond anticipated smaller losses due to fermentation during the week-end. Both in the A.P.C. and in the S.D. processes it would be necessary to keep over hot, nearly neutral juice for the same period and it was difficult to see why fermentation would be less for the clarifiers filled with neutralised and heated supernatant liquid than for the clarifiers filled with sulphited mixed juice.

Mr. Dymond stated that it was essential that the A.P.C. floc should not be disrupted after formation, hence the necessity for the rapid acidification by aqueous or liquid SO_2 to the desired pH. The suggested use of a sulphur tower, though imperfect,

could achieve this condition. Thereafter the floc could be affected by vibration, convection currents and the disturbance through filling. The design as shown in the paper counteracted these effects and had proved successful at Darnall.

Commenting on Dr. Douwes Dekker's figures, that the wax content of Oliver Campbell cake, plus the amounts found by him in the residual molasses, did not remotely check up with the amount of wax found in the first precipitate of the A.P.C. process, Mr. Dymond said he would have been surprised if it had been otherwise. In his paper last year he had shown how easily large amounts of wax disappeared during the natural fermentation of filter cake. In the same way the wax complex would tend to decompose and disappear during sugar fabrication.

With regard to the difference between the wax content of the samples of A.P.C. slurry sent to the C.S.I.R. and those now recorded, this was due to the different method employed. In the first, the precipitate was filtered but not washed, the sucrose and non-sugar content being high and the wax percentage consequently low. In the process described in the paper, these substances were removed first by washing on the Oliver filter and secondly by heavy dilution, boiling and resubsiding. The wax percentage rose accordingly and led to better retention and recovery.

Commenting on his claim that the A.P.C. process would lead to smaller fermentation losses over shut-downs, Mr. Dymond said that the present method of excess liming of the clarified juices before shutting down, merely increased acid fermentation losses by neutralising the acids as formed. In the A.P.C. process the cold sulphited juice would not be converted to clarified juice, but would remain at a low pH, when the SO_2 would act as an inhibitor of fermentation. A further advantage would be the efficient settlement of the first precipitate over such periods.

Dr. Douwes Dekker said that the clarifier would have to be kept filled with clear supernatant liquid and therefore the losses would be just the same as they were at present.

Mr. Dymond said that the juices would not be kept hot, but would be treated with SO_2 and kept cold. They would be converted to clarified juice after the shut down.

Dr. Douwes Dekker repeated that he was not referring to the clarifiers in which the acidified mixed juice was settled, but to those in which the limed supernatant liquid was settled.

Mr. Antonowitz said that any losses caused by fermentation would be increased by adding lime. For example, in the manufacture of food yeast, if the effluent which was discarded into the sewer

contained waste yeast or other micro-organisms it was impossible to control the acidity of this effluent merely by neutralising it with lime. Raising the pH to a point around 9.0 stimulated the activities of the bacterial population in the effluent neutralisation vessel so much that whereas originally for a given effluent pH, only one bag of lime was required, sometimes as much as twenty bags were required to be added before the effluent could be safely discharged. This difficulty was overcome by adding chloride of lime to the effluent in such concentration that "free" chlorine was present in the effluent; only then did the consumption of lime become normal. The principal point to be emphasised here is that if a drop in pH is experienced in juices held in storage, raising the pH by the addition of lime merely stimulated the activities of the micro-organisms, particularly the thermophiles and the added lime merely screens the drop in pH. Keeping the juice at a very low pH, viz. about 3.0, entirely suppresses bacterial activity.

The increase in acidity noted in juices kept at 95°C. over the week-end was probably due to enzymic activity and not strictly due to microbial activity. It was probably due to the adsorption of the enzymes by the precipitation of the proteins as effected by the acid pre-clarification process that losses would be eliminated.

Dr. Douwes Dekker enquired if Mr. Antonowitz had any evidence to show that enzymes were precipitated in the A.P.C. process.

Mr. Antonowitz replied that it was a practised commercial procedure in the recovery of certain enzymes and vitamins to absorb them by the precipitation of proteinaceous matter.

Mr. Carter said he could bear out the statement that juice at a high pH did not keep as well as juice at a lower pH, say at about 7 pH. He did not use phosphoric acid for a period of about five hours, prior to a shut-down, but the juice was acid and it appeared to keep much better than juice at 8 pH.

Dr. Van der Pol stated that he had found that with certain juices a precipitate could not be obtained at 2.8 pH or lower. As far as the amount of ash in the clarified juice was concerned, he could find little difference, from his experiments, when the A.P.C. process was compared with the conventional sulpho-defecation process. It was, however, a known fact that a cold sulphitation process lead to heavy incrustation of heating surfaces, due to supersaturation of the juice with respect to calcium sulphite, and thus it was not in general use. It was, therefore, most probable that even though the ash in clarified A.P.C. juice be not unusually high, calcium sulphite would still precipitate out on heating subsequent to clarification, since this precipitation was a very slow process.

Mr. Dymond said that he had found that as a general rule 3.2 proved the best pH for precipitating, but that by reducing the pH to 2.8 the second precipitate settled more readily. As far as the composition of the ash was concerned a high percentage of silica was precipitated together with iron, but the variation was so small over the two precipitates that he thought that the general idea of ash reduction

might well be discarded.

Mr. Carter asked what was the maximum temperature at which he carried out his process.

Mr. Dymond said that he had experimented with temperatures of 40° and could find no fermentation or any other loss. Atmospheric temperatures were those usually employed.