

of acid mercuric nitrate, the mixture shaken, 20 cc. of water added, again shaken and filtered after 5 minutes. To the filtrate an equal volume of picric acid is added when if gelatin or the soluble decomposition products from the sour cream are present, a precipitate is formed. This is the method mentioned in *Bulletin 107* of the U. S. Dept. of Agriculture.

In order, definitely, to determine the nature of this precipitate, proceed as follows: Cork test tube which should be a large one, and shake very thoroughly. In this way the gelatin picrate will coalesce and filtration be much more rapid. If possible allow to stand for some time after shaking; most of the liquid can then be siphoned off. The precipitate after being brought on to the filter is washed with water containing two to three drops of ammonium hydroxide to 100 cc. until the washings are slightly alkaline to litmus, and then with neutral water until the washings are neutral to litmus. This will remove all excess of picric acid. The precipitate is then transferred to a small beaker and 10 to 20 cc. distilled water added and heated to boiling. If the precipitate is very small in amount it need not be taken from the filter paper, but both can be boiled together.

Filter hot into a test tube. The filtrate will contain the gelatin picrate but not the precipitate derived from the proteids in the sour cream. Cool this filtrate and add an equal volume of picric acid, when, if gelatin was present in the original cream, a decided precipitate will be formed. When large amounts of gelatin are present the solution may become turbid on merely cooling.

In order to determine the delicacy of this method, 25 cc. of a 1 per cent solution of gelatin containing 0.25 gram of gelatin were added to 50 grams of sour cream. The sour cream thus contained only 0.5 per cent of gelatin, which had little thickening effect on it. By using 20 to 25 cc. of this cream instead of 10 cc. as above the presence of the gelatin could be determined with certainty. The above method has been in use in this laboratory for some time and has been found to work satisfactorily, provided the conditions described are obtained. Even smaller quantities of gelatin than this can, of course, be detected by using a larger amount of the original sample.

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A STUDY OF THE COMPOSITION OF CIDER VINEGARS MADE BY THE GENERATOR PROCESS

By L. M. TOLMAN AND E. H. GOODNOW

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When an investigation of the composition of cider vinegar was undertaken by the Bureau of Chemistry about four years ago, a study of the literature on the subject showed that the existing data were composed almost exclusively of analyses of vinegars made by the old barrel process. The authenticity of the two or three samples of generator vinegars reported was not beyond question because of the extreme difficulty of obtaining true samples of such vinegar. There was practically no analytical basis on which the purity

of a given cider vinegar could be determined, and only the most obvious adulterations or substitutions could be detected with certainty. Apparently authentic cider vinegars were reported as containing amounts of solids varying from 1.18 to 8.00 per cent of ash from 0.19 to 0.57 per cent with the other constituents in the same general proportions. A review of the extensive data on fermented ciders, however, showed no such wide variations in composition, and plainly indicated that this marked difference in the composition of cider vinegars was due not to a similar difference in the composition of the raw material, but rather to the method of manufacture. As a new and scientifically controlled process of manufacture had become widely established, and was the source of practically all of the "commercial" cider vinegar on the market, it seemed probable that the product prepared by this process might differ perceptibly from the "barrel" vinegars, and this study was projected with this idea in view.

The essential differences between the barrel method and the generator method of making cider vinegar will be apparent from a brief description of these processes. The conversion of apple juice into vinegar in the barrel was, until recent times, the generally accepted method in this country. Although no longer used for the preparation of cider vinegar in large amounts on a commercial scale, it is still very largely employed on the farm as the source of the family supply. The general procedure is as follows: The juice expressed from the apples is allowed to ferment in a barrel, usually of 40 to 50 gallons capacity, until practically all of the sugar has been changed into alcohol, and the resulting hard cider stored in some dark place, frequently a cellar, where the formation of acetic acid takes place gradually. Under the most favorable conditions the conversion into vinegar is slow. The long period of storage required gives opportunity for infection by harmful organisms, with the development of mal-fermentations, which frequently change the character and composition of the product to a marked degree. The conditions of storage, temperature, cleanliness of the barrel and surroundings are factors entering largely into the quality of the finished vinegar. The simplicity of the method as regards mechanical features is more than offset by the disadvantages of an uncontrolled acetification.

The rapid or generator process is carried on in this country in a very uniform practice which may be outlined as follows: Large quantities of apples are pressed and the juice collected in tanks, holding from 200 to 1,000 barrels where it is allowed to ferment until the sugar is almost completely removed. It is obvious that this alcoholic fermentation on a large scale in contrast to the fermentation on a small scale in the barrel, tends to produce a uniform product. The hard cider thus obtained is run over the generators, which consist of upright cylindrical tanks filled with beech shavings, corn-cobs, rattan, or some similar porous material saturated with strong vinegar. The alcohol is converted almost immediately into acetic acid. The entire process is under exact control, and

can be completed in a very short time compared with the old method. There is practically no opportunity for mal-fermentations to develop and their occurrence would be readily detected. Fully 90 per cent of the cider vinegar made on a commercial scale in the United States is manufactured by this generator process.

It was impossible to establish a fair standard for judging the purity of generator vinegars on the basis of the existing analytical data on barrel vinegars. Before such a standard could be established some data with reference to the composition of generator vinegars must be available and the changes taking place during this method of acetification clearly understood.

from the generators, thus practically establishing a chemical control of the manufacture. The amounts of cider and vinegar used for the feed were carefully measured so that its composition could be accurately calculated. By carrying this experiment over a period of about two months and running some 40,000 gallons of cider over the generators, some interesting and conclusive figures were obtained.

At the beginning of this experimental run the shavings in the generators were saturated with vinegar made from the cider used in the previous run just completed. Before vinegar representative of the new tank of cider could be obtained, it was, therefore, neces-

TABLE I—ANALYSES OF CIDERS AND VINEGARS FROM TANKS 1 AND 2

	Date	Alcohol by volume per cent	Solids, Grams per 100 cc.	Total Fehling reducing bodies, Grams per 100 cc.	Total sugars as invert Grams per 100 cc.	Non-sugars, Grams per 100 cc.	Ash, Grams per 100 cc.	Alkalinity of ash, Cc. N/10 acid per 100 grams	Total acids as acetic Grams per 100 cc.	Fixed acids as malic Grams per 100 cc.	Ash in non-sugars Per cent	Pentosans, Grams per 100 cc.	Glycerol, Grams per 100 cc.
CIDER AND VINEGAR													
Tank 1:													
CIDER:													
First day's run.....	Jan. 18	7.9	3.05	0.57	2.48	0.34	39.0	0.48	0.15	13.7	0.153	0.31
Eighth day's run.....	Jan. 25	7.8	3.09	0.58	2.51	0.35	39.8	0.50	0.18	13.9	0.156	0.29
Eleventh day's run.....	Jan. 29	7.8	3.09	0.58	2.51	0.35	39.2	0.48	0.17	13.9	0.158	0.31
Fourteenth day's run.....	Feb. 1	7.8	3.07	0.57	2.50	0.34	38.6	0.46	0.19	13.6	0.165	0.30
Vinegar from previous run used to start this tank, generated	Jan. 17	0.38	2.45	0.69	0.43	2.02	0.34	35.6	5.75	0.04	16.8	0.176	0.27
VINEGAR:													
First day's drip.....	Jan. 18	0.40	2.48	0.58	0.41	2.07	0.34	36.4	5.73	0.04	16.4	0.179	0.28
Third day's drip.....	Jan. 20	0.41	2.56	0.59	0.41	2.09	0.34	36.8	5.72	0.05	16.2	0.176	0.27
Sixth day's drip.....	Jan. 23	0.45	2.54	0.63	0.45	2.09	0.33	37.6	5.71	0.05	15.8	0.180	0.29
Eighth day's drip.....	Jan. 25	0.40	2.59	0.68	0.48	2.11	0.34	36.8	5.91	0.05	16.1	0.181	0.28
Tenth day's drip.....	Jan. 27	0.46	2.70	0.70	0.50	2.20	0.33	37.4	5.85	0.06	15.5	0.180	0.27
Thirteenth day's drip.....	Jan. 30	0.46	2.76	0.70	0.52	2.24	0.33	36.6	5.76	0.06	14.7	0.195	0.29
Sixteenth day's drip.....	Feb. 2	0.42	2.79	0.74	0.55	2.25	0.34	37.2	5.76	0.07	15.1	...	0.28
Tank 2:													
CIDER:													
First day's run.....	Feb. 3	7.75	2.78	0.37	2.41	0.35	38.4	0.50	0.19	14.5	0.120	0.30
Ninth day's run.....	Feb. 11	7.7	2.76	0.36	2.40	0.35	36.8	0.48	0.20	14.6	0.111	0.31
Fourteenth day's run.....	Feb. 16	7.6	2.73	0.35	2.38	0.35	36.6	0.48	0.20	14.4	0.114	0.31
Seventeenth day's run.....	Feb. 19	7.6	2.72	0.33	2.39	0.38	39.6	0.52	0.22	13.8	0.118	0.29
VINEGAR:													
Second day's drip.....	Feb. 4	0.43	2.81	0.77	0.56	2.25	0.35	37.2	5.74	0.08	15.5	0.183	0.28
Eighth day's drip.....	Feb. 10	0.43	2.79	0.73	0.53	2.26	0.36	38.4	5.80	0.07	15.9	0.175	0.28
Thirteenth day's drip.....	Feb. 15	0.40	2.80	0.72	0.53	2.27	0.36	38.8	5.98	0.06	15.9	0.178	0.29
Seventeenth day's drip.....	Feb. 19	0.37	2.78	0.72	0.52	2.26	0.35	38.4	6.02	0.07	15.5	0.172	0.29
Vinegar made from following tank	Feb. 27	0.35	2.69	0.69	0.49	2.20	0.33	38.4	6.02	0.07	15.0	0.161	0.27

Accordingly, arrangements were made with a favorably situated cider vinegar factory where the so-called "single-run" generator system was used. In this system the cider is mixed with a slightly larger quantity of strong vinegar to reduce the alcoholic content of the feed to such an extent that a single passage through the generator would completely convert the alcohol in the mixture into acetic acid. This factory was so arranged that all of the 60 generators in operation were fed from a central supply tank system and all of the finished vinegar was collected in one central receiving tank. Thus by determining the composition of the cider and vinegar which were mixed to supply the generators, and finally of the vinegars produced, the changes taking place during the conversion of cider into vinegar could be closely followed.

In a small laboratory established at the factory, certain determinations, such as solids, ash, sugar, acidity, alcohol and color, were made. Each day samples were taken of the cider, of the vinegar used to mix back for the feed and of the finished vinegar coming

sary that this vinegar should be completely displaced. As 3 or 4 barrels of vinegar were held absorbed in the packing material of each of the generators, several days would be required before such displacement would normally occur. Another factor which would retard the securing of a vinegar characteristic of this tank of cider lay in the method of feeding the generators. The cider stock was not fed "straight," but instead first mixed with a slightly larger volume of vinegar. For the first day's feed, January 18, vinegar from the drip of January 17 was used for this "mixing back," and each day the vinegar for this purpose was taken from the drip of the preceding day. With this system, it can readily be seen that considerable time must elapse before the vinegar dripping from the generators would be characteristic of the cider stock being fed, especially if there was much difference in the composition of the cider stock and of the vinegar from the previous tank.

In the preceding table a sufficient number of analyses of the ciders and vinegars taken at intervals during

the running of Tanks 1 and 2 has been given to show the changes in composition observed. Each tank contained about 20,000 gallons of cider which was practically of constant composition from the first pumpings to the last, so that for the purpose of comparison a slight variation need not be considered.

Although the vinegar produced on the first day of the experimental run, January 18th, did not differ perceptibly from that of the previous day, decided changes were noted as the operations continued. The total acidity showed a good average yield of acid and remained nearly constant for the entire period, varying only 0.3 gram during the run of the two tanks. Less than 0.5 per cent alcohol remained unconverted in the finished vinegar coming from the generators.

The fixed acids are noticeably affected by the acetification process. The cider of Tank 1 contained about 0.15 gram fixed acids and the vinegars mixed back for the feed 0.04 gram, so that the feed had a fixed acid content of about 0.10 gram. The vinegar coming from the generators contained 0.04 gram fixed acids, and, although the amount increased to 0.08 gram as the run progressed, due to a similar proportional increase in the fixed acid content of the cider, there was a loss of approximately 60 per cent in the generators. This elimination of fixed acids during the acetification process is shown graphically by the curves in Fig. 1.

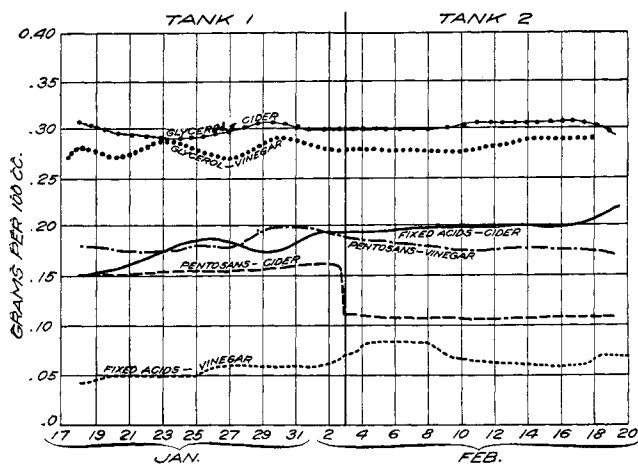


FIG. 1.—VARIATIONS OF FIXED ACIDS, PENTOSANS, AND GLYCEROL DURING CONVERSION OF CIDER INTO VINEGAR

There appears to be a very uniform and constant loss during acetification. In this respect the generator method produces effects similar to the barrel process, in which the fixed acids gradually disappear during the conversion of the cider into vinegar. As the sweet cider probably contained from 0.3 to 0.4 gram of fixed acids, it is apparent that the loss of fixed acids in both the alcoholic and acetic fermentations is very large.

The most notable change was in the content of solids. The first day's drip showed 2.48 grams while the feed had 2.72 grams, calculated from the proportions of carefully measured cider and vinegar used, and the cider itself 3.05 grams. Thus the vinegar coming from the generator contained 0.24 gram less solids than the feed running onto the generator, and 0.57 gram less than the cider stock. This apparent reduction of

solids in the generator during the acetification process is readily accounted for when the mechanical features of the process are taken into consideration. In each of the 60 generators at least 200 gallons of vinegar were held in the shavings, making approximately 12,000 gallons of vinegar in the series of generators at the start. To each generator every day were fed 40 gallons of mix, containing approximately 18 gallons of cider. The vinegar of this mix had practically the same composition as the vinegar in the generators, the vinegar from the previous day's drip being used for making up the feed. Thus each day a 40-gallon

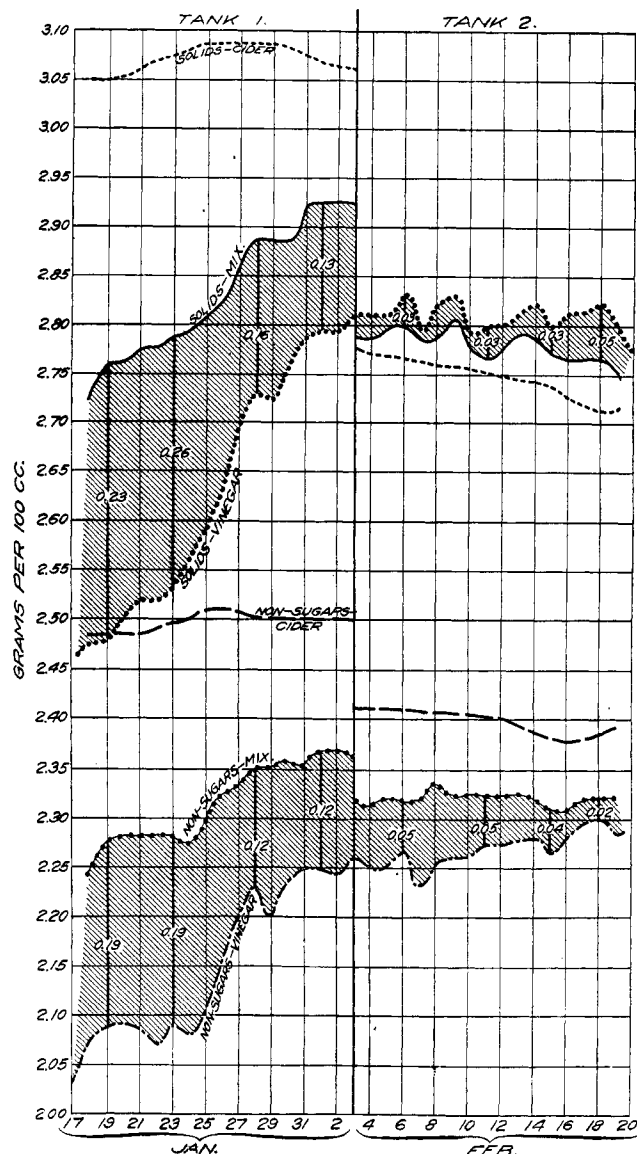


FIG. 2.—CURVES FOR SOLIDS AND NON-SUGARS

feed containing only 18 gallons of the cider was run into at least 200 gallons of vinegar in the generator, and 40 gallons of this mixture dripped out. Consequently only a slight change in the composition of the vinegar dripping from the generator could be expected from day to day, because of the comparatively small volume of the cider fed. When it is borne in mind that there were but 20,000 gallons of cider in Tank 1

and at least 12,000 gallons of vinegar to be displaced in the generators before a vinegar truly characteristic of this cider could be obtained, besides the retarding effect of mixing back each day with a more than equal amount of vinegar from the drip, it is evident that the changes observed must be gradual. That such was the case is shown by the analyses given in Table I and the curves in Fig. 2.

It will be noted that the solids in the vinegar showed an almost uniform daily increase, gradually approaching the solids content of the cider. At the end of 17 days' run on this tank, when the last of the cider had been fed on, the vinegar of the drip contained 2.79 grams solids, an increase of 0.31 gram during the run of this tank, or an average increase of nearly 0.02 gram per day.

The following tank of cider was much lower than the first in solids, having a content of 2.78 grams. The vinegar dripping from the generators contained 2.81 grams solids and the mix for the first day of the run, February 3, 2.78 grams. Thus at the beginning of the run of this tank the solids content of the mix being fed to the generators was practically identical with both that of the vinegar soaked in the shavings, and the cider stock being used, in sharp contrast with the wide differences noted at the start of the run of Tank 1. Were there any appreciable loss of solids in the generator during the acetification process, it would be plainly apparent under these conditions.

From the analyses given in Table I and the curves in Fig. 2, it will be noted that the solids content of the vinegar was almost constant during the run of this tank, and very slightly in excess of the solids in the mix, showing conclusively that there is no appreciable loss of solids in the generation of vinegar by this method. The variations observed in the running of Tank 1 were due mainly to the lag caused by the mixing back with vinegar of a different composition and by the large amount of vinegar of a different composition in the generators when the experiment began. The results indicate that if Tank 1 had been much larger, containing perhaps 40,000 gallons, and the experiment could have been continued for two weeks longer, a vinegar of practically the same composition as the cider would have come from the generator. This is shown clearly by the curves for the solids in Fig. 2. In the case of Tank 1, where the solids of the cider and of the vinegar soaked in the generator, varied widely, there is a decided rise in the curves for both vinegar and mix, these two curves approaching each other. In the case of Tank 2, in which the solids of the cider and the vinegar retained in the generators were practically the same, the curves show no appreciable change during acetification.

The variations in the non-sugar solids during acetification were similar to those already noted in case of the total solids. The cider of Tank 1 had a non-sugar content of 2.48 grams, while the vinegar from the previous day's drip and the vinegar which was absorbed in the filling material of the generator contained only 2.02 grams of non-sugars, and the mixture of cider and vinegar run onto the generators con-

tained 2.22 grams. Thus at the beginning of the experimental run the vinegar coming from the generator and retained in the generator contained about 0.2 gram non-sugars less than the mix fed to the generators and 0.46 gram less than the non-sugar solids in the cider. As the run progressed the non-sugars in the finished vinegar increased gradually, as will be seen from the curves in Fig. 2, approaching the amount present in the feed; but this increase is not quite as rapid as the increase in the total solids.

In the case of Tank 2, the non-sugar content of the cider was 2.41 grams, and that of the vinegar coming from the generator 2.25 grams, so that the mixture of the two going onto the generator contained 2.33 grams. During the run the non-sugar solids in the drip increased very slightly, the vinegar containing 2.26 grams at the end of the run or only about 0.05 gram less than the mix being fed on, but it is probable that this slight loss is more apparent than real. The non-sugars are the resultant of the difference between the total solids and the total sugars, calculated as invert sugar, and any error in the determination of either of these constituents would affect the result for the non-sugars. The total sugars are determined after inversion by their reducing power on Fehling solution. There is present in cider vinegars a substance formed during the acetification which reduces alkaline copper solutions, and thus interferes with the estimation of the sugars by the usual reduction method. Attention was called to the presence of this substance by Mr. Balcom, associate referee on vinegar, in his report to the Association of Official Agricultural Chemists. It was, of course, necessary to modify the method for determining the sugars to eliminate the reducing effect of this substance, which was easily accomplished as it is volatile and readily distilled off by repeated evaporations of the vinegar to a small volume on a steam bath. The following procedure was adopted for the determination of the sugars: 50 cc. of the vinegar were evaporated on the steam bath to 10 cc., and two additions of 10 cc. water with subsequent evaporations to 10 cc. made. This solution was then made up to volume and the reducing sugars determined in the usual manner. From the difference between the Fehling reduction of the vinegar direct and after evaporation, the volatile reducing bodies can be approximated quantitatively in terms of their reducing power. A direct determination can also be made on the distillate from vinegar. For this purpose 100 cc. of the vinegar were distilled down to 10 or 15 cc., 100 cc. of water added and a second distillation made, the two distillates being kept separate. The Fehling reduction was made on the distillates and on the residue made back to volume, following the same procedure as in the determination of invert sugar. The results calculated to grams invert sugar from the Fehling reduction for a few samples of the vinegars from these runs are given in Table II.

It is quite apparent that the presence in vinegars of a substance with a reducing power equivalent to 0.15-0.20 gram invert sugar would cause an appreciable error in the determination of the sugars, and conversely,

TABLE II—FEHLING REDUCING BODIES
(Calculated as invert sugar)

Vinegar of	Direct after inversion Grams per 100 cc.	After evaporating 3 times, Grams per 100 cc.	On residue from distil- lation, Grams per 100 cc.	Distillate			Total reducing bodies in residue and dis- tillate Grams per 100 cc.
				First 100 cc. Grams per 100 cc.	Second 100 cc. Grams per 100 cc.	Total Grams per 100 cc.	
Jan. 22.....	0.62	0.45	0.44	0.13	0.01	0.14	0.58
Jan. 23.....	0.65	0.45	0.46	0.15	0.01	0.16	0.62
Jan. 24.....	0.66	0.48	0.48	0.14	0.01	0.15	0.63
Jan. 28.....	0.68	0.50	0.52	0.13	0.02	0.15	0.67
Feb. 6.....	0.77	0.56	0.55	0.16	0.01	0.17	0.72
Feb. 8.....	0.77	0.56	0.56	0.16	0.02	0.18	0.74
Feb. 11.....	0.73	0.53	0.55	0.14	0.01	0.15	0.70
Feb. 13.....	0.73	0.53	0.53	0.14	0.02	0.17	0.70
Feb. 17.....	0.73	0.52	0.53	0.16	0.02	0.18	0.71

the non-sugars, by the Fehling reduction method. Our subsequent work on cider vinegars has shown that these bodies are frequently present in still larger amount. Although their exact composition has not been determined, they appear to be of an aldehyde nature, not acetaldehyde as might be inferred from its close relation to ethyl alcohol and acetic acid, but some more complex derivative.

The examination of daily samples of the vinegars made in these experimental runs showed an average of 0.18 gram of these volatile reducing bodies calculated as invert sugar in the finished vinegar, while in the ciders there are none. The formation of these bodies in the generation of vinegar has undoubtedly given rise to the idea that there is an increase in sugars during the process of converting cider into vinegar. In all probability this error in the determination of the sugars is the explanation of the abnormally low non-sugar solids occasionally reported in analyses of vinegars made a number of years ago. After carefully correcting for the amount of volatile reducing bodies present, there actually appears to be a slight increase in the amount of sugar present in the vinegar, as determined by reduction, over that present in the cider.

During the experimental run the total sugars in the vinegar made from Tank 2 decreased from 0.56 to 0.52 gram, while the mixture fed onto the generators contained 0.47 gram, showing a slight increase of sugars which can be accounted for only on the ground of the actual development of reducing bodies. This increase is probably due to the increase in pentosans, which was particularly noticeable in the run of Tank 2, the cider of which contained 0.12 gram of pentosans, while the vinegar coming from the generators contained 0.18 gram, an increase of nearly 50 per cent (see Fig. 2). The small amount of invert sugar present in the fermented cider is not appreciably affected during the acetification, nor are the ash, the ash constituents, or the alcohol precipitable bodies noticeably influenced by the passage through the generator. There is an appreciable loss of color, which, however, largely returns to the vinegar on storage. This loss of color was not observed in the experimental runs with other kinds of generators in other factories; apparently it is associated with the small-sized type of generator used in this plant. The glycerol content of the cider and of the finished vinegar remained practically con-

stant throughout the whole experimental run, as will be seen by noting the curves of Fig. 1. The difference between the glycerol in the cider and in the finished vinegar is very slight, and as this variation is undoubtedly due partly to the factor of the vinegar introduced from the previous run the actual loss in acetification is negligible.

The actual yield of acid was almost constant throughout the run, although considerably below the theoretical yield. Theoretically, 1 part by weight of alcohol or 1.26 parts by volume of alcohol should yield 1.304 parts by weight of acetic acid. As the cider of Tank 1 contained approximately 7.85 per cent by volume of alcohol and 0.23 gram per 100 cc. of acetic acid, the theoretical yield would be calculated as follows:

CALCULATION OF ACID YIELD

Tank 1

	Grams of acetic acid
Theoretical yield:	
7.85 per cent alcohol by volume in cider.....	8.12
Acetic acid in cider.....	0.23
Total.....	8.35
Yield in practice:	
Average of vinegar for run.....	5.75
Actual yield is 68.9 per cent of theoretical yield	

Tank 2

	Grams of acetic acid
Theoretical yield:	
7.60 per cent alcohol by volume in cider.....	7.87
Acetic acid in cider.....	0.31
Total.....	8.18
Yield in practice:	
Average of vinegar for run.....	5.78
Actual yield is 70.6 per cent of theoretical yield	

These calculations and all comparisons between the ciders and vinegars have been made without allowing for any loss in volume by evaporation in passing through the generator. Under normal conditions of working, the loss from this source is not material.

The percentage of ash in the non-sugar solids of the cider in Tank 1 was 13.7 and of the vinegar at the start 16.8. Only fractional variations in this ratio were observed during the run of this tank, and the drip at the end contained 15.1 per cent of ash in the non-sugars. The cider in Tank 2 contained 14.5 per cent

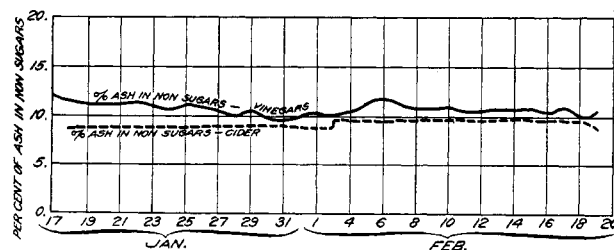


FIG. 3—PERCENTAGE OF ASH IN NON-SUGARS

of ash in the non-sugars, and the vinegar during the run varied from 15.5 to 15.9 per cent. The slightly higher percentage of ash in the non-sugars of the vinegar was undoubtedly due to the slight apparent loss of non-sugars during acetification already discussed in connection with the increase in pentosans and total Fehling reducing bodies. There appears to be a very constant relation between the amounts of non-sugar

solids and ash which is of decided value in detecting the addition of ash material in the case of adulterated or imitation vinegars. The curves showing the variations in this ratio for these runs have been plotted in Fig. 3.

CONCLUSIONS

The results of this investigation show conclusively that vinegar manufactured by the generator process is uniform in its composition; as uniform as the cider—from which it is prepared—in which respect it differs materially from the vinegars manufactured by the old barrel process. With the exception of the conversion of the alcohol into acetic acid there is but little change in the composition of the cider as it is being converted into vinegar. The most marked difference, other than the oxidation of the alcohol into acid, is the elimination, or, perhaps, destruction of the fixed acids. Here there appears to be an almost constant loss during acetification. On the other hand, there is a considerable formation of pentosans in the generator. No appreciable loss in solids or non-sugars takes place, and the other constituents are practically unaffected. The amount of glycerol in the cider remains almost unchanged by its passage through the generator, and, as it is a product of the alcoholic fermentation, it is an important factor for the detection of adulteration in commercial vinegars. The percentage of ash in the non-sugar solids is remarkably constant, varying only within slight limits, and is of decided value as a standard for judging the purity of cider vinegars.

The results indicate plainly that, given the composition of a hard cider to be used in the manufacture of vinegar by the generator process, it is possible to approximate very closely the composition of the vinegar which can be made from it.

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ON THE DECREASE OF AVAILABLE PHOSPHORIC ACID IN MIXED FERTILIZERS CONTAINING ACID PHOSPHATE AND CALCIUM CYANAMID

By R. N. BRACKETT
Received July 25, 1913

About two years ago one of the fertilizer companies in this state found that one of their brands ran deficient in available phosphoric acid, although it was thought that ample provision had been made in overage for that ingredient. A representative of the company stated that calcium cyanamid had been used as one of the ingredients of his mixture. As this material usually contains an excess of free lime it appeared possible that the cause of the deficiency in available phosphoric acid in his goods might be traceable to the fact that the soluble or the reverted phosphoric acid had been to some extent converted into insoluble.

Preliminary experiments¹ on mixtures containing cyanamid showed that there was a slight decrease of available, due to the increase of the insoluble over that calculated for the mixture.

In the early spring of 1912 a mixer in a near-by town made up a mixture to analyze: 10 per cent available

phosphoric acid, 4 of ammonia and 4 of potash, using calcium cyanamid as one ingredient of his mixture. His formula was as follows:

	Pounds
Acid phosphate, 16 per cent.....	1250
Calcium cyanamid.....	200
Dried blood.....	250
Muriate of potash.....	175
1/2 and 1/2 mixture (composed of 1/2 16 per cent acid phosphate and 1/2 C. S. meal, damaged).....	125
	2000

Upon having this mixture analyzed in a commercial laboratory it was found to be deficient in available phosphoric acid. We received a sample through a purchaser, and also found it deficient in available phosphoric acid, analyzing about 8-4-4, instead of 10-4-4. At our request this mixer consented to send us samples of the materials above mentioned.

Before these materials were received, we made up a mixture¹ of an acid phosphate and cyanamid, using the proportions given above. The acid phosphate used gave as an average of six analyses:

	Per cent
Total phosphoric acid.....	18.37
Water-soluble phosphoric acid.....	13.58
Insoluble phosphoric acid.....	1.74

On a 0.3 gram sample, the cyanamid analyzed 14.97 per cent of nitrogen.

The mixture consisted of 250 grams of the acid phosphate and 40 grams of cyanamid, a ratio of one part of the cyanamid to 6.25 parts by weight of the acid phosphate; the initial temperature of the materials was 21° C. and upon mixing the temperature increased to 32° C.

RESULTS (ZERBST AND HUTSON)

	Phosphoric acid—Per cent			
	Total	Water-soluble	Insoluble	Available
Original acid phosphate.....	18.37	13.58	1.74	16.63
Analysis of the mixture, calculated, if no change on mixing....	15.84	11.71	1.50	14.34
Average of five analyses, 5 days after mixing.....	15.82	3.96	1.58	14.24
Average of three analyses, 12 days after mixing.....	...	3.54	1.69	14.13
Average of four analyses, 19 days after mixing.....	...	3.45	1.78	14.04
Average of six analyses, 26 days after mixing.....	2.28	13.54
Average of two analyses, 33 days after mixing.....	2.75	13.07
Average of three analyses, 40 days after mixing.....	3.21	12.61
Average of three analyses, 47 days after mixing.....	3.57	12.25
Work discontinued at end of 47 days.				

These results would appear to indicate that the conversion of the water-soluble or of the dicalcium phosphate to tricalcium is not simply a function of the temperature and of the alkalinity of the cyanamid, as is held by some, but that the element of time is perhaps of equal importance with the temperature. Hence it might well happen that a mixture freshly made up would show the required and desired amount of available, and yet be found deficient when analyzed some weeks later. The results of this experiment

¹ Made by L. D. Boone. Results not available.

¹ This work was done by G. H. Zerbst and H. M. Hutson.