Aug. 28, 1934. W. J. BANNISTER 1,972,059

PRODUCTION OF ORGANIC ACIDS BY THE ALKALINE FUSION OF CELLULOSIC MATERIALS

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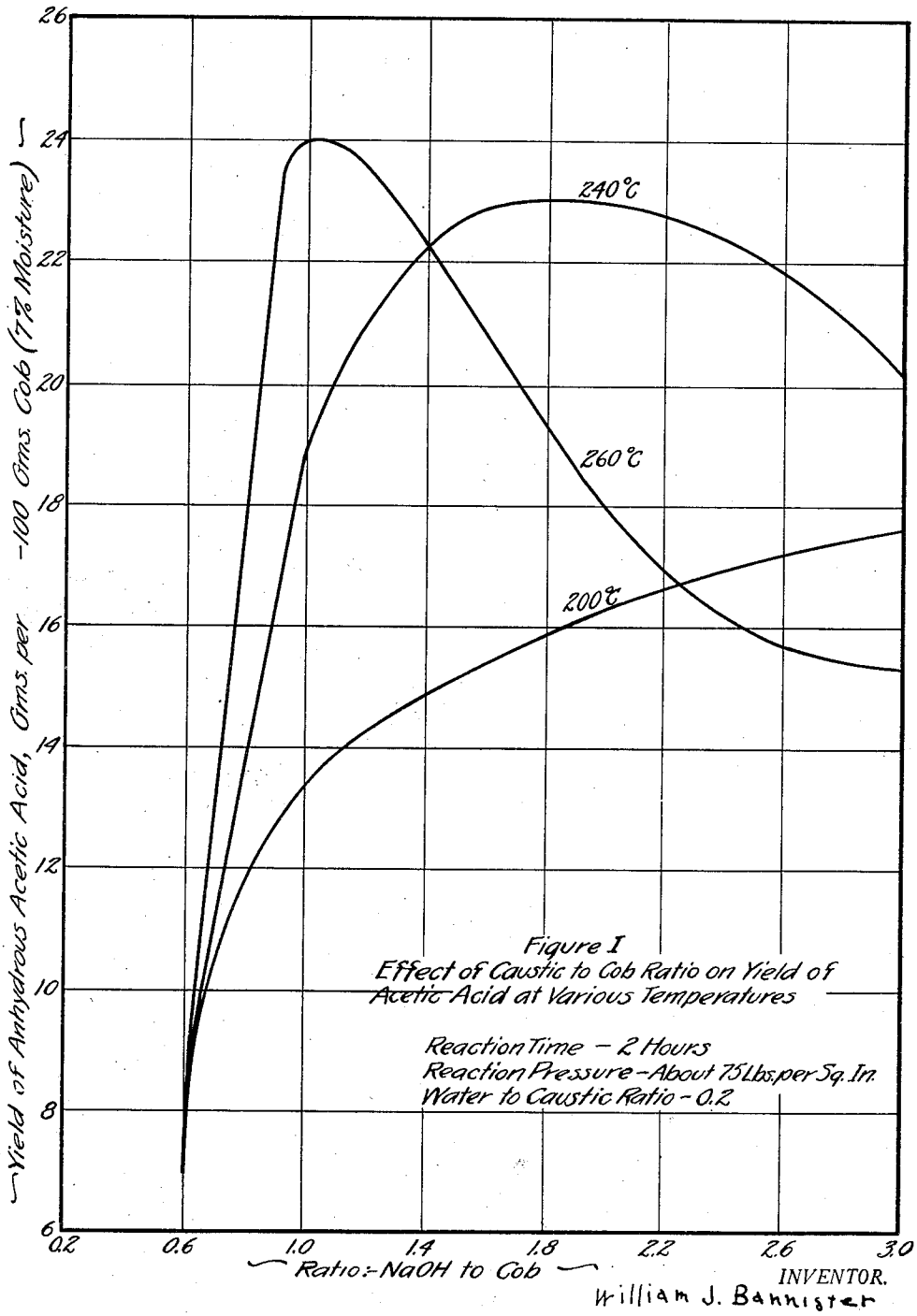


Figure I
Effect of Caustic to Cob Ratio on Yield of Acetic Acid at Various Temperatures

Reaction Time – 2 Hours
Reaction Pressure – About 75 Lbs. per Sq. In.
Water to Caustic Ratio – 0.2

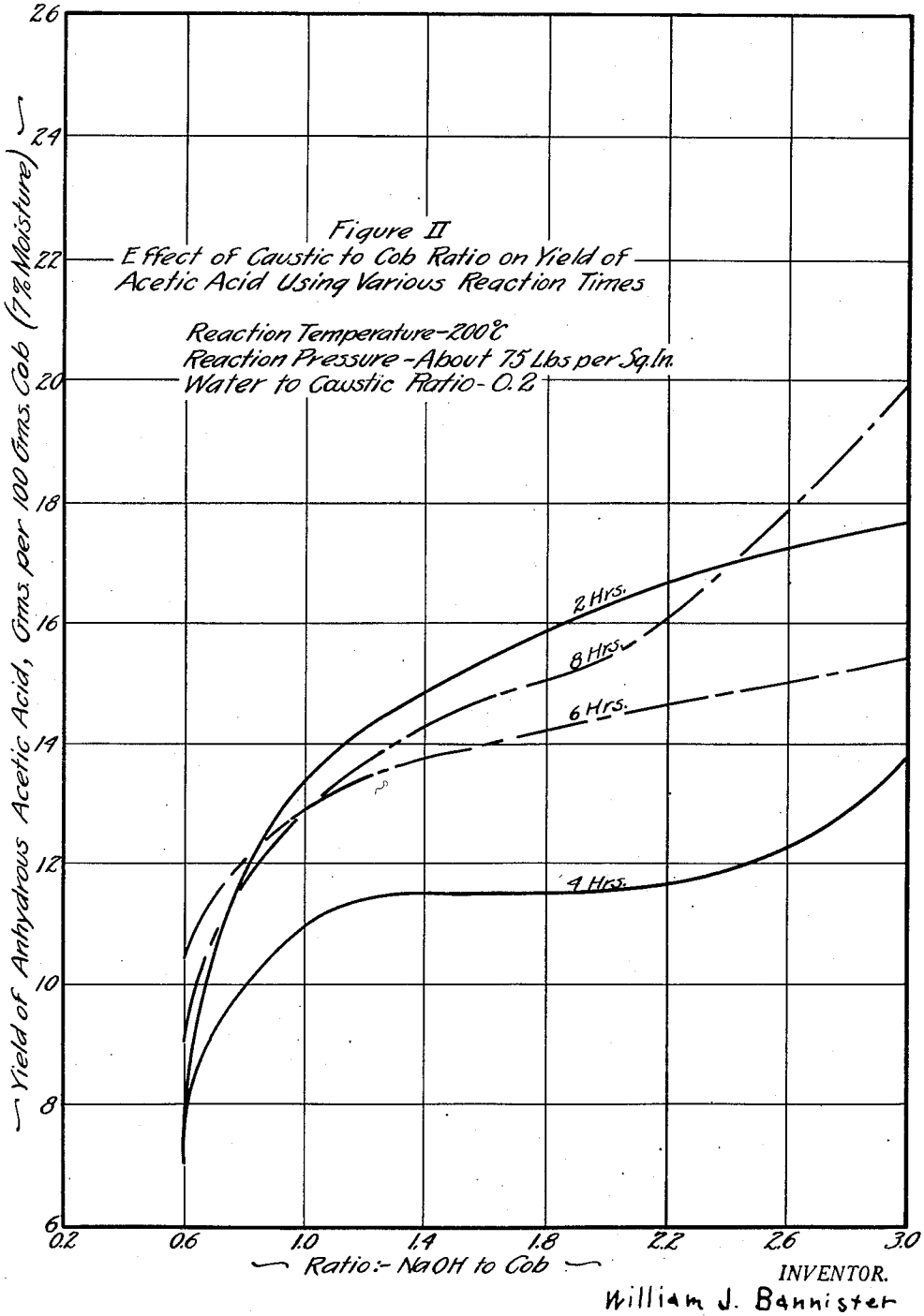
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1,972,059

PRODUCTION OF ORGANIC ACIDS BY THE ALKALINE FUSION OF CELLULOSIC MATERIALS

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5 Claims. (Cl. 260—119)

The present invention relates to a method for the production of organic acids from cellulosic materials, and more particularly to the production of acetic acid from cellulosic materials such as corncobs.

Considerable work has been done in the past—especially by Sweeney and his coworkers—on the production of organic acids by the alkaline fusion of corncobs. The efforts of these workers, however, have been directed chiefly towards the utilization of material of this character as a substitute for wood in the production of oxalic acid. The formation of acetic acid during this operation was reported but it was only regarded as a by-product of some promise which might serve to reduce the cost of producing the oxalic acid and no methods of obtaining optimum yields of the former were described. The production of organic acids other than acetic and oxalic was not reported by these investigators, nor has any other investigator disclosed a process whereby acids such as acetic, oxalic, formic, succinic, etc. can be obtained by the alkaline fusion of cellulosic materials.

The method recommended by previous workers for the production of oxalic acid by the alkaline fusion of corncobs consisted of treating ground corncobs with two and one-half times their weight of caustic soda in a suitable vessel. A small amount of water was added and the mixture stirred and heated. Heat was controlled very carefully to avoid charring and the temperature brought very slowly up to 200° C. When the mass turned a lemon yellow color, the fusion was stopped and allowed to cool. The mass was then lixiviated by a counter-current method for the recovery of the products formed. The treatment from this point on was to fractionally crystallize the oxalate and acetate of sodium, remove the oxalate and treat with lime to obtain the original sodium hydroxide and calcium oxalate. This calcium oxalate was then treated with sulphuric acid to obtain pure oxalic acid.

By carrying out the alkaline fusion of corncobs and other cellulosic materials according to the method hereinafter described, difficulties experienced by previous investigators are largely overcome, and at the same time it is possible to obtain larger yields of total acids and larger yields of acids of greater value and of much wider commercial application than formerly. Previous investigators, who have generally been interested in obtaining maximum yields of oxalic acid, have experienced considerable difficulty due to the charring of the cellulosic material at the temperatures required by the reaction. Another distinct disadvantage of such processes has been the large excess of alkali which it was found necessary to employ. These disadvantages are largely overcome in my improved process. In addition, the yields of acetic acid—a product of considerably greater commercial importance than oxalic acid—are much higher, and at the same time considerable quantities of oxalic, formic and succinic acids are obtained. Small quantities—1% or less—of higher acids such as butyric, propionic, etc., are also produced.

I have discovered that improved yields of acids and especially of acetic acid may be obtained by making use of somewhat higher temperatures than recommended by previous investigators, by increasing the length of time required for the reaction, by carrying out the fusion under pressure, and by decreasing the ratio of caustic to cob, previous recommendations being that a much greater caustic to cob ratio must be used in order to obtain maximum yields. My process consists essentially of fusing cob meal or other suitable forms of cellulosic material with the required amount of caustic soda and small amounts of water. In carrying out the fusion it has been found that best results are obtained if the temperature of the mixture is quickly raised to the reaction point (160°—280° C.) and then held at this point for a predetermined time. The heating is carried out in a closed vessel and under pressure, thus avoiding danger of too rapid dehydration of the charge and spontaneous ignition. A gas formed as a reaction product, and consisting largely of hydrogen, is permitted to escape through a safety valve or pressure regulator, set to hold the pressure at any desired point. At the conclusion of the reaction, the melt is treated for the recovery of the organic acids which are present in the form of their sodium salts. One of the distinct advantages of my process enters into play at this point since other investigators have frequently encountered difficulty in filtering the melt due to the presence of colloidal material. Little or no difficulty is experienced in this respect when conducting the fusion according to the method which I have specified.

As has been previously indicated, I have found that the production of the maximum yields of acids depends at least in part on the ratio of caustic to cob, the ratio of water to caustic, the temperature, and the duration of the reaction. The ratio of the particular acids formed appears

also to be dependent at least in part on the ratio of caustic to cob and the temperature of reaction. By the term "ratio of caustic to cob" is meant the relative amount in parts by weight of caustic and cob employed. For example, the ratio "0.6" means that caustic and cob were present in the ratio of six parts by weight of caustic to ten parts by weight of cob. The term "ratio of water to caustic" is similarly employed. In the discussion of results which follows, the time of reaction expressed is the length of time which the charge is held at the reacting temperature after having been brought up to that temperature.

As the result of an extensive series of experiments in which the factors mentioned above have been varied over a fairly wide range, it has been found that altho both the total yields of acids and the relative proportions of these acids may be changed, variations of the latter type are probably the more marked. In the case of acetic acid, I have found that with a caustic to cob ratio of 0.6, the yield is independent of the temperature and reaction time within the limits of 200° and 260° C. and 2 to 8 hours. However, as shown in Figure I, for a given period of time the effect on yield of changing the caustic to cob ratio varies with the temperature. At 200° C. the yield of acetic acid grows as the ratio of caustic to cob is increased between 0.6 and 3.0; at 240° C. the yield reaches a maximum at the caustic to cob ratio 1.8 and falls off as the latter is further increased, and at 260° C. the maximum yield is obtained at a ratio of caustic to cob of about 1.0.

As stated above, the time factor has little or no influence on the acid yield at a caustic to cob ratio of 0.6. On the other hand, at higher ratios (see Figure II) the yields for the 2 and 8 hour runs are highest, the yield for the 4 hour run is lowest and that for the 6 hour run is intermediate.

Runs were also made at a time of eleven and one-half hours. In this instance, the temperature was slowly raised to 240° C. in the course of nine and one-half hours, instead of the usual one hour, and then maintained there for two hours. The yields rose sharply to a maximum at the caustic to cob ratio of 0.8, and then fell abruptly.

Generalizations for the yields of formic acid cannot be made, as in no case do the yields follow any orderly course, very wide and sharp variations occurring under each of the conditions discussed above. Apparently these variations in yields are due to the fact that formic acid is converted to oxalic acid with the liberation of hydrogen, and various factors cause this reaction to take place in some cases more than in others. Best yields were obtained at 200° C. and two hours time with caustic to cob ratios of 0.8, 2.0 and 3.0; at 200° C. and six hours time a ratio of 1.0 gave optimum results; at 240° and two hours time a ratio of 0.9 was found most desirable; with the temperature remaining at 240° C. and the time increased to four or six hours, the optimum ratio was found to be 1.3; at the slow heating at 240° C. during the eleven and one-half hour intervals, the optimum caustic to cob ratio was found to be 0.9. These represent the best yield points obtained. In general, however, the yield of formic acid diminishes as the concentration of caustic soda becomes greater, as the duration of the run becomes longer, and as the temperature of the reaction increases.

Also, no generalizations can be made for the oxalic acid yields. Good yields were obtained with a caustic to cob ratio of 1.2 and an operating temperature of 200° C. maintained for two hours time; with a ratio of 2.0 at 260° C. and a ratio of 0.9 at 260° C., the reaction period being two hours in each of the latter cases. A low yield of formic acid was accompanied by a high yield of oxalic acid and vice versa, for the reason given above.

It is likewise difficult to make generalizations that will hold under all conditions concerning the amount of succinic acid produced. As a rule, however, it may be stated that when the proportion of acetic and formic acids is high, that of the succinic acid will be low and vice versa.

In carrying out my process it was found that some water must be present, and a water to caustic ratio of 0.2 to 0.6 was found to give optimum results. While the function of this water is not definitely known there are some indications that it reacts with the succinic acid as indicated by the following equation:

$$COONa(CH_2)_2COONa + 2NaOH + H_2O \rightarrow CH_3COONa + HCOONa + Na_2CO_3 + 2H_2$$

This would explain why the yield of acetic acid is high when that of succinic acid is low, and vice versa.

As will be readily seen from the preceding discussion, the relative proportions of the various products formed may be varied considerably simply by varying one or more of the operating conditions. In general, however, unless these factors are changed so as to remove them appreciably from the optimum operation conditions the total yields of organic acids will be fairly constant for different operating conditions and only the relative proportions of the several individual acids will be materially changed. A typical yield based on the weight of corncobs containing 7% of moisture is as follows:

	Per cent
Acetic acid	25
Oxalic acid	30
Formic acid	15
Succinic acid	10

These yields were obtained by carrying out the fusion with caustic soda in a closed container at approximately 75 pounds per square inch pressure, using a caustic to cob ratio of 1.0, a water to caustic ratio of 0.2, a temperature of 260° C. and a two hour period of reaction. By referring to Figure I it will be seen that these conditions represent approximately the optimum conditions for the formation of acetic acid for a 2 hour fusion. As illustrated by the results shown above, it has been observed that the acetic acid produced under any particular set of conditions usually amounts to about one-half the sum of the oxalic and formic acids.

The mechanism of the reactions involved in the alkaline fusion of cellulosic materials such as corncobs is of such a character that few statements of a conclusive nature can be made concerning it. It appears to me, however, that the first reaction taking place is the hydrolysis of the acetyl group of the non-cellulosic part of the corncob. This takes place if only water or alcohol is used with no caustic present, and amounts to a yield of acetic acid equivalent to about 5% of the cob.

The next reaction seems to be a breaking down of the cellulose molecule by the sodium hydroxide under the conditions employed, with the probable formation of the sodium salt of a complex intermediate acid in addition to the sodium salts of

acetic and formic acids. The formation and decomposition to sodium succinate and then to sodium acetate and formate of the intermediate compound would naturally be greatly affected by caustic concentration, temperature and time of reaction, and hence it is not surprising that these factors have a decided influence on the nature and yield of the final products.

It is believed that most of the oxalic acid produced in the reaction is not formed as a direct product of the decomposition of cellulose, but owes its origin to the decompostiion of formic acid:

$$2HCOOH- \begin{matrix} COOH \\ | \\ COOH \end{matrix} + H_2$$

The decomposition of the intermediate acid would constantly free new formic acid, a part of which may be decomposed sooner or later to oxalic acid. Thus, the irregularity of the yield of formic acid is explained, as is also the fact that in general the yield of formic acid is higher in runs at lower temperatures and at lower sodium hydroxide concentrations.

The above discussion gives a satisfactory working explanation, but it will be understood that it is not desired nor intended that it be construed as, nor limited in meaning to, the exact mechanism of the reaction involved in this present process.

The results obtained in numerous experiments indicate that the fusions should be conducted with low concentrations of caustic soda at a fairly high temperature and for a short period of time. The conditions most favorable for good yields are the following, it being understood that relatively slight variations therefrom are permissible.

Ratio of water to caustic	0.2–0.6
Ratio of caustic to cob	0.9–1.2
Temperature	255°–265° C.
Time	1–3 hours

Sodium hydroxide has been found to give better results in the fusion than any other of the common alkaline materials. The addition of other alkaline compounds or of auxilary inorganic oxidizing materials does not increase yields of the organic acids.

The yield of acetic acid is increased as the temperature is raised up to a certain limit. This limit rises as the sodium hydroxide concentration decreases.

In general, better results are obtained in short fusions than in long ones, but if the time of fusion is increased considerably, good yields of acetic acid are again obtained.

The cob meal need not be very fine, as fairly coarse material of about 5 to 8 mesh, gives equally good results.

Pressure is necessary for good results. However, 50 or 75 pounds pressure gives as good results as much higher pressures. The sole function of pressure in this instance seems to be to prevent too rapid dehydration of the cobs. Open pot fusions not only give poorer yields, but are extremely hazardous, due to the tendency for spontaneous ignition to occur.

In the data given in Figures I and II, the yield figures refer to the number of grams of anhydrous acids resulting from 100 grams of cob (moisture content 7%) charged. The sodium hydroxide used was about 93–95% NaOH, the rest being sodium carbonate and water.

The products of the fusion may be recovered by any of the known means for separating formic, acetic, oxalic and succinic acids from mixtures containing these acids.

The above description shows the procedure which I prefer to follow. Results were, however, also obtained by the use of the following common alkaline materials other than caustic soda, although the yields were small: lime, barium hydroxide, potassium hydroxide, lithium hydroxide, ammonium hydroxide, and mixtures of sodium and potassium hydroxides. In the last mentioned instance, the caustic potash did not increase the yields materially, and in the remaining instances, the yields obtained were always lower than when caustic soda was employed.

Also, there was substituted for the cobs, cellulosic materials other than that described above. For example, oat hulls, cotton waste, and fermented residue from the Langwell cellulose fermentation process, etc. were employed. The fermentation residues gave good yields, but in other cases the yields were low. All of these substitutions, however, fall within the concept of the present invention, and it will be understood that it is desired to include within the scope of this invention such modifications and changes as may be necessary to adapt it to varying conditions and uses.

As previously pointed out, the presence of liquids such as water, alcohol and the like are necessary for the production of efficient yields. The function of these compounds, however, is not clearly understood since it appears that their action is upon the cellulose as well as the non-cellulose ingredients of the cob or other material being employed. These liquids may be omitted altogether, and the reaction will proceed, but it may be pointed out that a certain amount of water will be produced as one of the products of the reaction, so that some effect of water will be manifest even if the water be originally absent from the mixture as formed. However, as previously mentioned, the presence of liquid in the aforesaid ratios is necessary for efficient results, and one of the effects of such liquid is probably the hydrolysis of amylaceous portions of the cob. Therefore, the liquids employed are defined in the claims by the term "hydrolyzing liquids", or equivalent expression but it will be understood that this expression is not intended as a limit of the function of these liquids since their action is in fact not clear, and may be even largely of a physical rather than of a chemical nature.

Now having described my invention, what I claim is:

1. In a process for the production of organic acids of the group consisting of acetic, formic, oxalic and succinic acids from cellulose-containing material, the improvement which comprises fusing said material with caustic soda at temperatures from 200–260° C. and under a pressure in excess of 50 lbs. per sq. in.

2. In a process for the production of acetic, formic, oxalic and succinic acids from cellulose-containing material, the improvement which comprises fusing said material with caustic soda in a ratio of caustic soda to cellulose-containing material ranging from 0.9 to 3.0, at temperatures from 200–260° C. and under a pressure in excess of 50 lbs. per sq. in.

3. In a process for the production of acetic, formic, oxalic and succinic acids from cellulose-containing material, the improvement which comprises fusing said material with caustic soda at temperatures from 200–260° C. and in an atmosphere comprising the gaseous reaction prod-

ucts of the fusion maintained under a pressure in excess of 50 lbs. per sq. in.

4. In a process for the manufacture of acetic, formic, oxalic and succinic acids from cellulosic materials, the improvement which comprises forming a mixture of caustic soda, cellulosic material and water in the ratio ranges of water to caustic soda of 0.2 to 0.6 and caustic to cellulosic material of 0.9 to 3.0, and rapidly heating said mixture in a closed container to a temperature range of 200° C. to 270° C., and maintaining said temperature for a period of one to three hours, and under a pressure in excess of 50 pounds per square inch.

5. In a process for the production of acetic, formic, oxalic and succinic acids from cellulosic materials, the improvement which comprises forming a mixture of caustic soda, cellulosic material and water in the ratio ranges of water to caustic soda of 0.2 to 0.6, and caustic to cellulosic material of 0.9 to 1.2, and heating said mixture in a closed container to a temperature range of 240° C. to 270° C., and maintaining said temperature for a period of one to three hours, and under a pressure in excess of 50 pounds per square inch.

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