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PRODUCTION OF ORGANIC ACIDS AND SALTS THEREOF FROM CELLULOSIC MATERIALS

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This invention relates to the production of organic acids and salts thereof, and more particularly to a process of producing said materials wherein a mixture of cellulosic material and an aqueous alkaline solution is heated in a closed system.

It is well known that a number of organic acids can be produced by heating various cellulosic materials with alkali and alkaline solutions. For example, it is known that sodium acetate and sodium formate are formed in the soda and sulphate wood pulping processes; that oxalic acid can be made by the alkaline fusion of cellulosic materials; and that lactic acid can be produced by the action of caustic soda on simple sugars. In our copending applications Serial Numbers 318,531 and 318,532 filed November 3, 1952 we disclose that black liquor from the sulphate wood pulping process contains substantial quantities of sodium lactate and sodium glycolate in addition to the previously known sodium salts of acetate and formate.

As set forth in the present invention we have further discovered that the salts of acetic, formic, lactic and glycolic acids can be produced from a variety of cellulosic materials, simultaneously and in improved yields over these obtained in said wood pulping process. Furthermore, we have discovered a process for producing these acids and salts thereof in which the formation of undesirable organic materials is substantially reduced.

An object of the present invention is to provide a process for producing organic acids and their salts. A further object is to provide such a process characterized by high yields, simplicity and economy. Other objects will be apparent from the description of this invention given hereinafter.

The above and other objects are accomplished according to this invention by carrying out the herein described process of producing saturated monocarboxylic acids having 1–3 carbon atoms in which one of the hydrogen atoms on the carbon atom adjacent the carboxyl group may be substituted by an hydroxyl group, which comprises subjecting a mixture of cellulosic material and an aqueous alkaline solution to a temperature of 250° C.–300° C. in a closed system, acidifying the reaction mixture and thereby obtaining a mixture of said acids in aqueous solution. Among the acids which form, formic, acetic, lactic and glycolic are of primary interest according to this invention. If the salts of the said acids are desired, the above acidification step is omitted. Although this invention is applicable to the production of organic acid salts, for the sake of simplicity and clarity it will be described for the most part with reference to the production of organic acids.

Cellulosic or so-called ligno-cellulosic materials in general are applicable to this invention, typical examples of which include wood, bark, straw, bagasse, sericea, pure cellulose, and the like, It is known that formic, acetic and lactic acids can be produced from simple sugars, such as glucose, by treatment with alkali at temperatures obtainable under atmospheric pressure. It is considered that the cellulose and hemicelluloses in cellulosic materials probably break down into simpler carbohydrates which are capable of yielding organic acids under the hydrolytic conditions of this invention. It is known that oxalic acid is the major product obtained by heating a substantially dry mixture of cellulosic material and alkali in the presence of oxygen. The formation of oxalic acid does not occur to any substantial extent during the process of this invention.

Lignin in the cellulosic material does not contribute significantly to the yield of the desired organic acids, but it is known that lignin will react with sodium hydroxide to give phenols and a variety of other materials which may be by-products in the present invention.

We have found that substantially pure cellulose under the process of this invention will yield the four desired acids, however it is much less preferred than the other raw materials disclosed herein. It appears that the hemicellulose content of the cellulosic material is an important contributing factor to the yield of acids obtained during the process of this invention. Therefore, in addition to economic reasons, we prefer to use a starting material such as wood, bark, straw, etc. Thus the term "cellulosic material" is used herein to cover, in addition to cellulose per se, materials which contain other carbohydrates of the type commonly classified as hemicellulose.

The process of our invention requires that the cellulosic materials be reacted with alkali and water in the liquid phase, therefore the alkali required may be broadly defined as an aqueous alkaline solution. It is preferred to use an alkali selected from the group consisting of water soluble hydroxides and carbonates of alkali metals and alkaline earth metals. The sodium compounds are preferred for reasons of economy, however, potassium and lithium compounds are approximately equal in their reactions to the sodium compounds. Barium hydroxide is a suitable alkali but its cost renders it less attractive. Calcium hydroxide is less desirable than the sodium compounds because of its lower water solubility.

The above definition of suitable alkalies is also intended to include impure alkaline solutions such as the spent liquor from alkaline wood pulping processes commonly known as "black liquor," partially spent liquor from the process of this invention which may be refortified or used as is in succeeding cooks, and other similar impure solutions containing suitable alkali.

Preferably either sodium hydroxide or sodium carbonate solutions will be used, and which one of these is used will depend on the specific results desired. Sodium hydroxide is less selective than sodium carbonate as regards the constituents of cellulosic materials with which it will react. It is known that even below 200° C. sodium hydroxide is capable of reacting with lignin to render it soluble in aqueous alkaline solution. We have found that under the conditions of our invention practically all of the wood becomes soluble in sodium hydroxide. Several of our experiments show this, e. g. in several instances in which a mixture of oak sawdust and sodium hydroxide was heated at 260° C., the insoluble residue remaining at the end of the cook amounted to only 6%–9% of the initial weight of the wood. If in addition to the organic acids one desired to obtain phenolic materials (e. g. catechol) from lignin, sodium hydroxide or other alkali metal hydroxide may be used.

It has been found according to this invention that sodium carbonate possesses certain advantages over sodium hydroxide. About the same yields of acids, based on wood, can be obtained with either alkali. This is quite unexpected, because sodium hydroxide is much superior to sodium carbonate in the conventional process of producing oxalic and acetic acids from wood by the action of alkalies. Another advantage in using sodium carbonate is that it costs less than sodium hydroxide. Sodium carbonate also possesses certain other advantages over sodium hydroxide in our invention from a process standpoint.

Sodium carbonate gives acids of a higher purity. For example, when a mixture of wood and sodium carbonate is cooked at 260° C. for one hour, the amount of insoluble residue that remains is about 26%–35% of the wood initially used as compared with only about 6%–9% when sodium hydroxide is used. Thus when sodium hydroxide is used a larger amount of the undesired materials is associated with the sodium salts of the desired organic acids in solution. Acidifying the solution to liberate the acids from their salts and removing the undesirable residue leaves a mixture of the desired acids in aqueous solution regardless of which alkali is used, but it is more difficult to purify these acids when sodium hydroxide is used. They may be purified by conventional solvent extraction or they may be purified and separated by one of the processes disclosed in our copending applications referred to hereinbefore. The fact that this large amount of residue remains indicates that sodium carbonate is relatively inert toward those components of the wood which are not involved in producing the desired acids. Consequently less of the sodium carbonate is used up in side reactions than is the case with sodium hydroxide, thereby leaving more of the sodium carbonate available for producing the desired acids.

Another advantage of using sodium carbonate as compared with sodium hydroxide relates to the ease of recovery and reuse of excess alkali. This is especially true if the acids are purified by employing the process disclosed in the first of our above mentioned two copending applications.

The process of said copending application involves treating concentrated alkaline liquors of the sodium salts of the desired organic acids with alcohols to precipitate certain impurities and leave the sodium salts of said acids in a more nearly pure state in the alcohol solution. Any sodium carbonate that remains in solution is precipitated from the alcohol and therefore is not present to consume mineral acid when it is used to liberate the organic acids from their salts. Since sodium carbonate is much less soluble in alcohol than is sodium hydroxide, it can be removed more completely and thus permit an important economy. The organic matter precipitated by the addition of alcohol and that which is in the form of a precipitate at the end of the cook, contains some sodium. When this organic matter is burned, e. g. in a pulp mill recovery furnace, to recover its heat value, the soda is recovered as sodium carbonate which can be re-used directly in the process of this invention.

Another favorable source of alkali is the black liquor that results from alkaline pulping processes such as the soda or sulfate process. Black liquor contains, in addition to the organic materials which have dissolved in the liquor during pulping, appreciable amounts of sodium hydroxide and sodium carbonate. Black liquor from the sulfate process also contains some sodium sulfide which is an efficient source of alkali for this invention. As pointed out hereinbefore, black liquor already contains appreciable amounts of the desired organic acids.

As would be expected, the use of black liquor as a source of alkali is advantageous to the extent of its content of alkali and the desired organic acids. We have found that black liquor also contributes advantages in addition to those normally expected. The amounts of lactic and glycolic acids formed during cooking are larger than would be expected from treatments under similar conditions with equivalent amounts of sodium hydroxide and sodium carbonate. A further advantage in using black liquor as a source of alkali is that during the cook there is a very favorable precipitation of undesirable organic matter from the black liquor so that the solids obtained at the end of the cook may be greater than the weight of the wood at the start. This precipitate is easily removed by simple filtration.

The reaction of our invention is carried out at a temperature of 250° C.–300° C. The temperature employed

is critical. Below 250° C. the yields are undesirably low. Above 300° C. a substantial part of the acids produced, except acetic, is destroyed. Among other things, Example 4 hereinafter shows the role of temperature. A temperature of 260° C.–280° C. has been found to produce the best results.

Within quite broad limits reaction time is not a critical factor, however a period of about one hour has been found to be most satisfactory under most conditions. A substantial amount of acids is obtained after cooking only 15 minutes at 260° C. Cooking in excess of an hour produces no marked increase in yield.

The Examples hereinafter give a number of illustrations of the effect the amount of alkali used has on yield of acids. The manner in which the yield of acids varies with the amount of alkali used depends on what basis is used to determine yields. In general the following conclusions are true. If acid yields are based on wood used, they vary directly with the amount of alkali used. If acid yields are based on alkali used, they vary inversely with the amount of alkali used. The data in Table 8–A of Example 8 hereinafter support these conclusions. Technically it does not matter whether an excess of alkali is used, but economically the amount of alkali used will depend on the relative cost of wood and alkali. Ratios of wood to alkali will be chosen that will give the lowest possible cost of production. If waste wood is used, acid yields based on alkali will be of greater significance than the yields based on wood, and desirably one will use lower amounts of alkali rather than aiming for the maximum possible yields based on wood.

When black liquor is used, within obvious limitations dependent on the relative amounts of black liquor and waste wood available, it is more economical to operate at higher ratios of alkali to wood. To a certain extent black liquor is a cheap source of alkali, provided a large part of its soda is eventually returned to the pulp mill recovery system in a form suitable for preparing fresh pulping liquor. Since a large part of the soda will be returned as sodium sulfate, this will determine the amount of black liquor which may feasibly be used for the purposes of this invention. The reason for this is that although addition of a certain amount of sodium sulfate to the pumping process is desirable, there is a limit beyond which it is impractical to go.

It is important that water be present in the liquid phase during the cooking or heating period. Therefore cooking must be carried out in a closed system and of course under the autogenously developed pressure at the temperature employed. Although the presence of liquid water is essential, the amount is not critical. We have obtained best results with about 7 to 8 volumes of aqueous solution to one part by weight of wood. Smaller volumes are satisfactory but give somewhat lower yields of acids. Larger volumes may be used but it is economically undesirable because of the needless expense in providing larger equipment for handling the excess water.

When operating with the preferred volumes, the concentration of the desired acids in the cooking liquor is about 30–35 grams per liter when wood is being treated with sodium hydroxide or sodium carbonate. We have found that this concentration can be increased to at least 100 grams per liter by re-use of the cooking liquor from one cook as makeup solution for the next cook. Example 6 hereinafter illustrates this. If black liquor is used as alkali, the extent to which the cooking liquor can be reused to build up the concentration of acids depends on the concentration of black liquor used. Usually one would obtain the black liquor at a point in the pulp mill recovery system just after the tall oil soap has been removed, and this black liquor contains about 300–325 grams of solids per liter. At this concentration no further dilution is necessary, and after a single cook it contains about 90 grams per liter of the desired acids. When starting with this concentration of black liquor, normally

it is not as desirable to increase the concentration of the desired acids by re-use of the cooking liquor as it is when using other alkalies, as described above, because the concentration of acids is already quite high and because it is difficult to maintain the desired ratio of water to wood. However, if more concentrated black liquor is initially used, the concentration of acids can be further increased by re-use of cooking liquor without interfering with using the preferred water to wood ratio.

The following examples illustrate specific embodiments of this invention, but the invention is not limited thereto except as defined in the appended claims. In the examples, per cent is by weight.

Four different apparatus were used in carrying out the experiments disclosed in the examples. The apparatus used is specified in each example. One type apparatus was a one liter, stainless steel, electrically heated autoclave equipped with a stirrer. Another apparatus used was the same as that just described except its size was five gallons. Another type was a three gallon, steel, gas fired autoclave with no stirrer. Still another type of apparatus comprised three separate containers each made of one 1800 milliliter iron tube and immersed in water in a three gallon steel autoclave with no stirrer. With the latter type apparatus it was possible to simultaneously make three cooks and to make them under more nearly identical conditions than with separate cooks. The type apparatus used is given merely for completeness of disclosure and not in an attempt to show that the invention is limited thereby or by any other particular apparatus. While the type of apparatus which one uses may have some bearing on the results one obtains, from the results we have obtained one would not be justified in recommending a particular type of apparatus as being substantially better than another. In any event, the selection of any one of a number of specific types of useful apparatus for practicing this invention is well within the purview of those skilled in the art.

In the examples and elsewhere herein, the amounts of formic, acetic, lactic and glycolic acids were determined by the partition chromatographic method described by Marvel and Rands in the Journal of the American Chemical Society, 72, 2642 (1950).

EXAMPLE 1

The data in Table 1 below show the yields of acids obtained by cooking oak sawdust with sodium hydroxide at 260° C. The wood was mixed with the aqueous solution of sodium hydroxide and the mixture placed in a pressure vessel and heated. Runs 1, 2 and 3 were made in an electrically heated steel bomb with agitation. Runs 4 and 5 were made in a three gallon gas fired autoclave without agitation. At the end of the pressure cook, the amount of insoluble solid amounted to only 6%–9% of the starting weight of the wood. After heating, the pressure vessel was cooled to a temperature below 100° C., opened and the contents filtered to remove the small amount of insoluble material present. A portion of the filtrate was then acidified with sulfuric acid to liberate the free organic acids and the acidic solution was analyzed for the four desired acids.

Table 1

Run No.	Wood, grams	NaOH, grams	GME [1] NaOH per 100 grams wood	Vol., ml.	Time @ 260° C., hrs.	Percent yield based on Wood			
						Acetic	Formic	Lactic	Glycolic
1	50	14.8	0.74	350	2	4.6	7.0	13.2	[2]
2	50	80	4.0	400	2	9.4	7.0	8.8	8.2
3	50	9.3	.47	350	2	4.2	4.1	8.2	9.4
4	400	118.4	.74	3,000	1	4.1	8.4	8.2	6.1
5	400	150	.94	3,000	1	3.8	8.8	8.7	7.9

[1] GME is gram molecular equivalent.
[2] Amount of glycolic acid was not determined.

EXAMPLE 2

Ten runs, using sodium carbonate as the source of alkali, were made in the same manner as described in Example 1. The data are summarized in Table 2 below. Oak sawdust was used in each run and in each run the temperature was 260° C. Runs 1–3 were made in an electrically heated steel bomb with agitation. Runs 4–10 were made in a three gallon gas fired autoclave without agitation.

Table 2

Run No.	grams Wood	grams Na_2CO_3	GME Na_2CO_3 per 100 grams wood	Vol., ml.	Time, Hrs.	Residue, percent of Wood	Percent Yield based on Wood			
							Acetic	Formic	Lac.	Gly.
1	50	25	0.47	350	2	[1]	4.5	7.2	9.9	9.1
2	50	100	1.9	350	2	[1]	[1]	8.4	9.8	8.7
3	50	37.5	0.71	350	2	[1]	3.5	6.7	9.6	9.2
4	400	200	0.47	3,785	1	24	3.8	7.8	9.9	9.2
5	400	160	0.38	3,000	1	32	4.2	6.7	5.9	5.1
6	400	120	0.28	3,000	1	35	4.1	6.5	5.4	4.9
7	400	160	0.38	3,000	2	30	4.0	7.5	7.1	5.0
8	400	160	0.38	3,000	¼	48	3.6	5.4	4.4	3.4
9	400	200	0.74	3,785	2	22	4.5	8.4	7.8	6.3
10	400	200	0.74	3,000	1	45	4.2	7.4	6.2	6.0

[1] Value not determined.

EXAMPLE 3

In a series of runs, hardwood sawdust was cooked with various amounts of black liquor from a sulfate pulping process. The black liquor was taken from the pulp mill recovery system after it had been concentrated sufficiently to permit removal of tall oil soap. The liquor contained 400 grams of solids per liter. By titration of a diluted sample of black liquor with standard acid, it was found that 10.4 ml. of 0.5169 N HCl was required to bring the pH of 5 ml. of the black liquor to pH 8.3. From this value, it was calculated that each liter of black liquor contained an amount of available alkali equal to 1.075 molecular equivalents of NaOH. The organic acids content of the black liquor was found to be 8.7, 16.3, 11.1, and 9.5 grams per liter respectively of acetic, formic, lactic, and glycolic acids. In one run, black liquor was cooked directly without addition of sawdust. In the other runs, oak sawdust was mixed with the black liquor.

The mixtures were heated in a three gallon gas fired autoclave without agitation. After cooking, the charge was allowed to cool, the reaction mixture was filtered and the filtrate was analyzed for content of desired acids. In all runs the time of heating was one hour and the temperature was 260° C. The data are summarized in Table 3 below.

Table 3

Run	1	2	3	4	5
Grams Oak Sawdust	0	100	400	400	400
Grams Black Liquor Solids	1,200	1,200	1,200	1,600	800
Vol. of Liquid (liters)	3	3	3	4	3
Grams Residue Obtained	139	240	531	683	452
Acetic Acid:					
Grams present after cook	31.2	30.3	47.5	49.8	31.2
Grams before cook	26.1	26.1	26.1	34.8	17.4
Grams formed during cook	5.1	4.2	21.4	15.0	13.8
Percent formed based on wood		4.2	5.4	3.8	3.5
Percent increase during cook	19.5	16.1	82.0	43.1	79.3
Formic Acid:					
Grams present after cook	50.6	47.0	74.0	86.6	51.3
Grams before cook	48.9	48.9	48.9	65.2	32.6
Grams formed during cook	1.7	−1.9	25.1	21.4	18.7
Percent formed based on wood		−1.9	6.2	5.4	4.7
Percent increase during cook	3.47	−3.9	51.3	32.8	57.4
Lactic Acid:					
Grams present after cook	50.1	50.7	71.4	73.2	48.9
Grams before cook	33.2	33.2	33.2	44.3	22.1
Grams formed during cook	16.9	17.5	38.2	28.9	26.8
Percent formed on wood		17.5	9.6	7.2	6.7
Percent increase during cook	50.9	52.7	115.1	65.2	121.3
Glycolic Acid:					
Grams present after cook	33.6	38.9	67.2	63.6	43.5
Grams before cook	28.5	28.5	28.5	38.0	19.0
Grams formed during cook	5.1	10.4	38.7	25.6	24.5
Percent formed based on wood		10.4	9.7	6.4	6.1
Percent increase during cook	17.9	36.5	135.8	67.4	128.9

Table 4

Run No.	Grams Wood	Grams Black Liquor Solids [1]	Temp., ° C.	Grams Present After Cook			
				Acetic	Formic	Lactic	Glycolic
1	50	160	200	4.2	8.0	6.4	4.8
2	50	160	250	5.1	7.1	8.7	7.7
3	50	160	295	6.5	5.9	9.0	5.2
4	50	160	320	8.1	4.0	4.3	0

[1] The black liquor solids, before heating, contained 4.2 grams acetic, 6.2 grams formic, 5.5 grams lactic, and 2.8 grams glycolic acids.

EXAMPLE 5

A number of different cellulosic materials were heated with sodium hydroxide and sodium carbonate solution separately under the conditions shown in Table 5 below. It will be observed that acetic, formic, lactic, and glycolic acids form in all cases but that the relative amounts vary somewhat, the most obvious difference being that a relatively pure cellulose gives lower ratios of glycolic to lactic acids. The three different types of equipment described more fully hereinbefore were used in the various runs. Runs 1–5 were made in an electrically heated one liter stainless steel autoclave with stirring. Run 12 was made in a three gallon, gas fired, steel autoclave without stirring. The other runs were made in 1800 ml. iron tubes immersed in water in a three gallon autoclave.

Table 5

Run No.	Grams Cellulosic Material	Grams Alkali	Vol., ml.	Time, Hrs.	Temp., ° C.	Yield: percent of cellulosic material			
						Acetic	Formic	Lactic	Glycolic
1	Oak sawdust, 50	25 Na_2CO_3	350	2	260	4.5	7.2	9.9	9.1
2	do	9.3 NaOH	350	2	260	4.2	4.1	9.1	9.4
3	Pine sawdust, 50	25 Na_2CO_3	350	2	260	3.2	4.6	9.6	8.2
4	Pine Bark, 50	25 Na_2CO_3	350	2	260	2.8	4.2	6.8	4.0
5	Pine Chips, 400	150 NaOH	3000	1	260	3.0	8.9	10.6	6.6
6	Sericea, 50	20 NaOH	300	1	260	4.8	8.0	9.5	7.0
7	do	40 NaOH	300	1	260	5.8	7.6	11.6	7.0
8	Cellulose, 50	20 NaOH	300	1	260	2.1	11.7	13.5	6.5
9	do	25 NaOH	125	1	260	2.6	10.2	12.6	6.2
10	do	25 Na_2CO_3	300	1	260	1.4	8.2	4.7	3.3
11	Cellulose, 400	200 Na_2CO_3	3000	1	260	1.7	10.8	8.4	6.0
12	Cellulose, 50	50 Na_2CO_3	300	1	260	1.6	9.4	8.2	6.0

EXAMPLE 4

A series of runs was made which show the effect of temperature on the amount of acetic, formic, lactic, and glycolic acids that form when oak sawdust is heated with black liquor from the sulfate pulping process. Concentrated black liquor containing 49.5% solids was used after being diluted with water to a volume of 500 ml. The ratio of sawdust to black liquor solids was 50 grams to 160 grams. The grams of organic acids originally present in the black liquor were: 4.2 acetic, 6.2 formic, 5.5 lactic, and 2.8 glycolic. The mixture of black liquor and sawdust was cooked in an electrically heated one liter bomb. The temperature was held at the indicated maximum temperature for two hours but the total time of heating varied depending on the time for heating and cooling the charge. The total time of heating was greater in the case of the higher temperature cooks. The data show that under these conditions the best yields of lactic and glycolic acids occur in the range of 250° C.–295° C. At higher temperatures, the yield of acetic acid increases but the other acids are partially destroyed with the result that after cooking at 320° C. for two hours the solution contains less formic, lactic and glycolic acids than were present in the black liquor at the start of the cook.

EXAMPLE 6

As described hereinbefore, in the production of acetic, formic, lactic, and glycolic acids by heating sawdust with aqueous solutions of alkali, it is possible to build up the concentration of acids by using the liquor from one cook in place of water for preparation of the alkaline solution. In a series of such cooks, the charge for the first cook was prepared by dissolving 160 grams of sodium carbonate in 3000 ml. of water. The resulting solution was mixed with 400 grams of sawdust and the mixture was heated for one hour at 260° C. in a three gallon steel autoclave without stirring. After heating, the mixture was filtered and the residue washed with a little water. The combined volume of filtrate and washings was slightly larger than the initial volume of alkaline solution. A portion of this solution was analyzed for its acid content and 3000 ml. of the solution, after addition of 160 grams of Na_2CO_3, was used for cooking another 400 gram portion of sawdust. As shown in Table 6 below, the concentration of said acids in the cooking liquor can be increased substantially in this manner. Contrary to expectation, viscosity of the solution does not increase appreciably, indicating that whatever derivatives of the wood

remain in solution must be of relatively small molecular weight.

The data in Table 6 give both the amounts of the acids formed during each cook and the total amount in the filtrate after each cook.

Table 6

Run No.	Times Recooked	Grams Residue	Ml. Filtrate	Amount of Acids in Grams							
				Acetic		Formic		Lactic		Glycolic	
				1	2	1	2	1	2	1	2
1	1	124	3,620	16.1	16.1	30.5	30.5	26.7	26.7	23.2	23.2
2	2	154	3,375	17.9	31.2	28.0	53.3	22.1	44.2	24.3	43.5
3	3	221	3,400	11.7	39.4	23.6	71.0	24.5	63.8	26.6	65.3
4	4	161	3,320	17.3	52.1	21.0	83.7	26.0	82.3	25.4	83.0
5	5	148	3,430	19.1	66.2	28.7	104.3	29.2	103.6	28.9	103.9
6	6	156	3,540	28.9	86.7	22.4	113.6	26.2	116.8	31.9	122.8

1. Formed in cook.
2. Total in filtrate.

EXAMPLE 7

This example shows the effect of temperatures on the yield of organic acids. In each run, 1600 grams of oak sawdust was suspended in 12,000 ml. of an aqueous solution containing 800 grams of sodium carbonate and heated for one hour at the indicated temperature in a 5-gallon electrically heated autoclave with agitation. After the indicated period of heating, the material was cooled to about 50° C.–60° C., the contents of the autoclave was filtered, and a portion of the filtrate was analyzed to determine the amounts of acetic, formic, lactic, and glycolic acids which are present in the solution in the form of their sodium salts. The data obtained in these tests are shown in Table 7.

Table 7

Run No.	Temperature, °C.,	Yield of Acids in Grams			
		Acetic	Formic	Lactic	Glycolic
1	260	65.5	133.7	92.4	97.3
2	270	78.0	154.3	133.8	141.9
3	280	71.0	139.0	130.0	137.0
4	295	70.2	123.1	127.5	133.2

EXAMPLE 8

This example shows generally the effect the amount of alkali has on acid yields. In each run, 1600 grams of oak sawdust was suspended in 12,000 ml. of aqueous solution containing the indicated amount of Na_2CO_3, and the mixture was cooked for one hour at 270° C. in a 5-gallon electrically heated autoclave with agitation. After the charge had cooled it was removed from the autoclave and filtered. A portion of the filtrate was analyzed to determine the amounts of each of the acids that were present as sodium salts. The data obtained are given in Table 8 below.

Table 8

Run No.	Grams Wood	Grams NA_2CO_3	Yield of Acids in Grams			
			Acetic	Formic	Lactic	Glycolic
1	1,600	533	66.4	115.7	94.6	84.5
2	1,600	640	69.3	127.2	99.4	88.2
3	1,600	1,067	74	156.0	123.4	121.3

In order to show more specifically the relationship between the amount of alkali and yield of product, the data in Table 8 were used to calculate the acid yields based on both wood and amount of Na_2CO_3 as shown in Table 8–A. This latter data are reported as grams of acid obtained per 100 grams of wood used, and grams of acid obtained per 100 grams of Na_2CO_3.

Table 8–A

Run No.	Ratio Wood: Na_2CO_3	Acetic		Formic		Lactic		Glycolic		Total	
		g./100 g. Wood	g./100 g. NA_2CO_3	g./100 g. Wood	g./100 g. Na_2CO_3	g./100 g. Wood	g./100 g. Na_2CO_3	g./100 g. Wood	g./100 g. Na_2CO_3	g./100 g. Wood	g./100 g. NA_2CO_3
1	3:1	4.15	12.46	7.23	21.70	5.91	17.75	5.28	15.85	22.57	67.76
2	2.5:1	4.31	10.83	7.95	19.88	6.21	15.53	5.51	13.78	23.98	60.02
3	1.5:1	4.63	6.95	9.75	14.65	7.75	11.64	7.63	11.46	29.76	44.70

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

What is claimed is:

1. Process of producing saturated monocarboxylic acids, or salts thereof, said acids having 1–3 carbon atoms in which one of the hydrogen atoms on the carbon atom adjacent the carboxyl group may be substituted by an hydroxyl group, which comprises subjecting a mixture of cellulosic material, alkali and water in the liquid phase, wherein water constitutes a major part of the liquid phase, to a temperature of 250° C.–300° C. in a closed system, and recovering said salts from the reaction mixture.

2. Process of producing saturated monocarboxylic acids having 1–3 carbon atoms in which one of the hydrogen atoms on the carbon atom adjacent the carboxyl group may be substituted by an hydroxyl group, which comprises subjecting a mixture of cellulosic material and an aqueous alkaline solution to a temperature of 250° C.–300° C. in a closed system, the ratio of water to alkali

and the ratio of water to cellulosic material being at least 3.5 to 1 and at least 4 to 1 respectively, acidifying the reaction mixture and thereby obtaining a mixture of said acids in aqueous solution.

3. Process of producing saturated monocarboxylic acids having 1–3 carbon atoms in which one of the hydrogen atoms on the carbon atom adjacent the carboxyl group may be substituted by an hydroxyl group, which comprises subjecting a mixture of cellulosic material and an aqueous alkaline solution to a temperature of 250° C.–300° C. in a closed system, the ratio of water to alkali and the ratio of water to cellulosic material being at least 3.5 to 1 and at least 4 to 1 respectively, removing any substantial amount of insoluble material from the reaction mixture, acidifying the reaction mixture and thereby obtaining a mixture of said acids in aqueous solution.

4. Process of producing saturated monocarboxylic acids having 1–3 carbon atoms in which one of the hydrogen atoms on the carbon atom adjacent the carboxyl group may be substituted by an hydroxyl group, which comprises subjecting a mixture of cellulosic material and an aqueous alkaline solution to a temperature of 250° C.–300° C. in a closed system, the ratio of water to alkali and the ratio of water to cellulosic material being at least 3.5 to 1 and at least 4 to 1 respectively, removing any substantial amount of insoluble material from the reaction mixture, acidifying the reaction mixture and thereby obtaining a mixture of said acids in aqueous solution, and separating the acids from each other.

5. Process of producing saturated monocarboxylic acids having 1–3 carbon atoms in which one of the hydrogen atoms on the carbon atom adjacent the carboxyl group may be substituted by an hydroxyl group, which comprises subjecting a mixture of cellulosic material and an aqueous alkaline solution to a temperature of 250° C.–300° C. in a closed system, the ratio of water to alkali and the ratio of water to cellulosic material being at least 3.5 to 1 and at least 4 to 1 respectively, removing any substantial amount of insoluble material from the reaction mixture, purifying the reaction mixture by solvent treatment, acidifying the reaction mixture and thereby obtaining a mixture of said acids in aqueous solution.

6. Process of producing formic, acetic, lactic and glycolic acids, which comprises subjecting a mixture of cellulosic material and an aqueous alkaline solution to a temperature of 250° C.–300° C. in a closed system, the ratio ranges of water to alkali and of water to cellulosic material being 3.5 to 37.5 and 4 to 30 respectively, acidifying the reaction mixture and thereby obtaining a mixture of said acids in aqueous solution.

7. Process of producing saturated monocarboxylic acids having 1–3 carbon atoms in which one of the hydrogen atoms on the carbon atom adjacent the carboxyl group may be substituted by an hydroxyl group, which comprises subjecting a mixture of cellulosic material and an aqueous alkaline solution to a temperature of 260° C.–280° C. in a closed system, the ratio ranges of water to alkali and of water to cellulosic material being 3.5 to 37.5 and 4 to 30 respectively, removing any substantial amount of insoluble material from the reaction mixture, acidifying the reaction mixture and thereby obtaining a mixture of said acids in aqueous solution.

8. Process of producing saturated monocarboxylic acids, or salts thereof, said acids having 1–3 carbon atoms in which one of the hydrogen atoms on the carbon atom adjacent the carboxyl group may be substituted by an hydroxyl group, which comprises subjecting a mixture of cellulosic material and an aqueous solution of an alkali selected from the group consisting of water soluble hydroxides and carbonates of alkali metals and alkaline earth metals to a temperature of 250° C.–300° C. in a closed system, the ratio ranges of water to alkali and of water to cellulosic material being 3.5 to 37.5 and 4 to 30 respectively, and recovering said salts from the reaction mixture.

9. Process of producing saturated monocarboxylic acids having 1–3 carbon atoms in which one of the hydrogen atoms on the carbon atom adjacent the carboxyl group may be substituted by an hydroxyl group, which comprises subjecting a mixture of cellulosic material and an aqueous solution of an alkali selected from the group consisting of water soluble hydroxides and carbonates of alkali metal and alkaline earth metals to a temperature of 250° C.–300° C. in a closed system, the ratio ranges of water to alkali and of water to cellulosic material being 10 to 25 and 7 to 10 respectively, acidifying the reaction mixture and thereby obtaining a mixture of said acids in aqueous solution.

10. Process of producing saturated monocarboxylic acids having 1–3 carbon atoms in which one of the hydrogen atoms on the carbon atom adjacent the carboxyl group may be substituted by an hydroxyl group, which comprises subjecting a mixture of cellulosic material and an aqueous solution of an alkali selected from the group consisting of water soluble hydroxides and carbonates of alkali metals and alkaline earth metals to a temperature of 250° C.–300° C. in a closed system, the ratio ranges of water to alkali and of water to cellulosic material being 10 to 25 and 7 to 10 respectively, removing any substantial amount of insoluble material from the reaction mixture, acidifying the reaction mixture and thereby obtaing a mixture of said acids in aqueous solution.

11. Process of producing saturated monocarboxylic acids having 1–3 carbon atoms in which one of the hydrogen atoms on the carbon atom adjacent the carboxyl group may be substituted by an hydroxyl group, which comprises subjecting a mixture of cellulosic material and an aqueous solution of an alkali selected from the group consisting of water soluble hydroxides and carbonates of alkali metals and alkaline earth metals to a temperature of 260° C.–280° C. in a closed system, the ratio ranges of water to alkali and of water to cellulosic material being 10 to 25 and 7 to 10 respectively, removing any substantial amount of insoluble material from the reaction mixture, acidifying the reaction mixture and thereby obtaining a mixture of said acids in aqueous solution.

12. Process of producing saturated monocarboxylic acids having 1–3 carbon atoms in which one of the hydrogen atoms on the carbon atom adjacent the carboxyl group may be substituted by an hydroxyl group, which comprises subjecting a mixture of cellulosic material and an aqueous solution of sodium hydroxide to a temperature of 250° C.–300° C. in a closed system, the ratio ranges of water to alkali and of water to cellulosic material being 10 to 25 and 7 to 10 respectively, removing any substantial amount of insoluble material from the reaction mixture, acidifying the reaction mixture and thereby obtaining a mixture of said acids in aqueous solution.

13. Process of producing saturated monocarboxylic acids having 1–3 carbon atoms in which one of the hydrogen atoms on the carbon atom adjacent the carboxyl group may be substituted by an hydroxyl group, which comprises subjecting a mixture of cellulosic material and an aqueous solution of sodium carbonate to a temperature of 250° C.–300° C. in a closed system, the ratio ranges of water to alkali and of water to cellulosic material being 10 to 25 and 7 to 10 respectively, removing any substantial amount of insoluble material from the reaction mixture, acidifying the reaction mixture and thereby obtaining a mixture of said acids in aqueous solution.

14. Process of producing saturated monocarboxylic acids having 1–3 carbon atoms in which one of the hydrogen atoms on the carbon atom adjacent the carboxyl group may be substituted by an hydroxyl group, which comprises subjecting a mixture of cellulosic material and an aqueous solution of black liquor to a temperature of 250° C.–300° C. in a closed system, the ratio ranges of

water to alkali and of water to cellulosic material being 10 to 25 and 7 to 10 respectively, removing any substantial amount of insoluble material from the reaction mixture, acidifying the reaction mixture and thereby obtaining a mixture of said acids in aqueous solution.

15. Process of producing formic, acetic, lactic and glycolic acids, which comprises subjecting a mixture of cellulosic material and an aqueous solution of sodium hydroxide to a temperature of 260° C.–280° C. in a closed system, the ratio ranges of water to alkali and of water to cellulosic material being 10 to 25 and 7 to 10 respectively, removing any substantial amount of insoluble material from the reaction mixture, acidifying the reaction mixture and thereby obtaining a mixture of said acids in aqueous solution.

16. Process of producing formic, acetic, lactic and glycolic acids, which comprises subjecting a mixture of cellulosic material and an aqueous solution of sodium carbonate to a temperature of 260° C.–280° C. in a closed system, the ratio ranges of water to alkali and of water to cellulosic material being 10 to 25 and 7 to 10 respectively, removing any substantial amount of insoluble material from the reaction mixture, acidifying the reaction mixture and thereby obtaining a mixture of said acids in aqueous solution.

17. Process of producing formic, acetic, lactic and glycolic acids, which comprises subjecting a mixture of cellulosic material and an aqueous solution of black liquor to a temperature of 260° C.–280° C. in a closed system, the ratio ranges of water to alkali and of water to cellulosic material being 10 to 25 and 7 to 10 respectively, removing any substantial amount of insoluble material from the reaction mixture, acidifying the reaction mixture and thereby obtaining a mixture of said acids in aqueous solution.

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