

UNITED STATES PATENT OFFICE

2,461,740

PROCESS OF MAKING ORGANIC ACIDS
FROM CARBONACEOUS MATERIALMyron Kiebler, Pittsburgh, Pa., assignor to Carnegie Institute of Technology, Pittsburgh, Pa.,
a corporation of PennsylvaniaNo Drawing. Application October 2, 1947,
Serial No. 777,579

7 Claims. (Cl. 260—515)

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This invention relates to a process of making organic acids from carbonaceous material. The term "carbonaceous material" as used herein means coal, coke, carbon blacks and pitch.

This application is a continuation-in-part of my application Serial No. 588,253 filed April 13, 1945, now abandoned.

Among the organic acids which may be produced according to my invention are the acids of aromatic or benzenoid type, such, for example, as mellitic acid, benzene pentacarboxylic acid, and the benzene tetra, tri and dicarboxylic acids; and aliphatic acids, as, for example, oxalic acid and acetic acid. All of the acids mentioned are soluble in water and are sublimable or distillable. In addition to the above named acids there are also formed acids of complex and unknown structure but of value in commerce.

In the preparation of commercially valuable organic acids from bituminous coal or other related carbonaceous material by oxidizing agents, it is necessary to convert from 20 to 50% of the carbon of the coal to carbon dioxide. With any given carbonaceous material, there is a correlation between the yield and nature of the acids formed and the fraction of the carbon of the coal converted to carbon dioxide. With the lower ratios of carbon dioxide, high yields of the dark colored, complex "humic acids" are recovered; with high ratios, the yield of acids decreases, the acids are lighter in color, of simpler chemical structure, and of greater value in commerce. The degree of oxidation which yields these light colored, simple and more valuable products can be attained by the use of chemical reagents such as fuming nitric acid or alkaline permanganate at atmospheric pressure and at temperatures of about 100° C., or by the action of oxygen, at elevated pressures and temperatures, on suspensions of coal in aqueous alkali.

According to the present invention, I employ a two-stage oxidation process in which the first stage preoxidizes the carbonaceous material to a form in which the material can be further oxidized to the stage desired. In the first stage, I employ a chemical oxidizing agent which operates at atmospheric pressure and which can be readily regenerated by reaction with air. In the second stage, I employ the high pressure elevated temperature reaction of oxygen gas in aqueous alkali.

Any acid or acid anhydride with suitable oxidizing properties which can be regenerated by air and recycled in the process can be employed, for

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example sulphur trioxide, oxides of nitrogen, or the acids formed by reaction of these compounds with water.

With sulphur trioxide the carbonaceous material is rapidly oxidized to an intermediate stage containing 30 to 50% of oxygen, carbon dioxide is evolved, and the sulphur trioxide is reduced to sulphur dioxide. By recovery of the sulphur dioxide and reoxidation to sulphur trioxide with air by well-known methods, the sulphur trioxide can be recycled in the process and merely acts as an activator for, and carrier of, atmospheric oxygen.

The primary oxidation product of the coal or other carbonaceous material prepared by this procedure does not differ in superficial appearance from the original carbonaceous material. It has, however, now been preoxidized to a state where it is soluble in aqueous alkali such, for example, as a solution of sodium hydroxide, potassium hydroxide, sodium carbonate or potassium carbonate, especially at elevated temperatures. The alkaline solution prepared in this way contains in suspension the ash of the coal and any difficultly attacked organic material. These can be removed by filtration, centrifuging or other suitable means and the resulting alkaline "humate" solution oxidized to the simpler, light colored, water soluble, organic acids desired by subjecting the alkaline solution to the action of oxygen gas at elevated temperatures and pressures in suitable equipment, such as a packed reactor up which oxygen gas at the required pressure moves counter-current to the alkaline humate solution.

In a similar manner, I may use in the first stage of the process oxides of nitrogen, such as, N_2O_3 or N_2O_5 or a mixture of these, or a solution of nitric acid. For instance, a 2 normal solution of nitric acid when contacted with bituminous coal under suitable conditions results in conversion of the greater part of the coal to an alkali soluble form. Carbon dioxide is evolved and the nitric acid is reduced to nitric oxide (NO) which can be reoxidized by the air and reconverted to nitric acid by well-known procedures. As in the previous example, the alkaline solution of the oxidized coal can be separated from ash and unattacked organic material by filtration, centrifuging or other suitable means and oxidation completed by the action of oxygen gas at elevated temperatures and pressures in the presence of the aqueous alkali.

The advantages of this two-stage process lie

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in the fact that a large fraction of the desired oxidation can be carried out by readily regenerated oxidizing agents, at normal pressures and moderate temperatures. For example, when a bituminous coal, such as Pittsburgh Seam, is treated with sulphur trioxide in a suitable apparatus at 200° C. in a ratio of approximately 7 grams of sulphur trioxide per gram of coal, 10 to 15% of the carbon of the coal is converted to carbon dioxide and the resultant solid oxidation product formed, which weights approximately the same as the starting coal, contains 25 to 35% oxygen. Since the total oxidation desired corresponds to reaction of 1 to 1.5 lbs. of oxygen per lb. of coal, it is evident that further oxidation of such a preoxidized product will require less time and will consume less oxygen, thus expediting greatly the second stage operations. Similar advantages accrue when oxides of nitrogen or nitric acid are employed.

Although the concentration of the alkaline solution used in the second stage of the process may vary over a considerable range, the best results are obtained when the aqueous alkaline solution has a concentration of 3 to 15 normal. In the second stage of the process, the temperature employed is preferably between 200° C. and 300° C. and the partial pressure of oxygen in the oxidizing gas in the second stage of the process is preferably between 100 and 1,000 pounds per square inch.

The following are specific examples of the process:

Example 1

One hundred parts by weight of -16 +20 mesh bituminous coal, containing approximately 75% carbon, are placed in a suitable lead-lined, horizontal, rotating reactor and, while being agitated, are subjected to the action of sulphur trioxide gas. The reactor is warmed by external heat until the temperature of the reaction mixture has reached 200° C. Due to the exothermic character of the reaction between sulphur trioxide and coal, this temperature can be maintained without the addition of external heat, simply by controlling the rate of input of the sulphur trioxide. The reaction is continued until approximately 750 parts by weight of sulphur trioxide gas have been added. The exit gases contain carbon dioxide, sulphur dioxide and some sulphur trioxide. These gases may be separated by suitable methods and the sulphur dioxide, after re-oxidation, is recycled in the process. Fifteen to twenty per cent of the carbon of the coal appears as carbon dioxide in the exit gases. After the required amount of sulphur trioxide has been added, air is blown through the reactor to remove any residual sulphur trioxide and to cool the reactor to room temperature. The oxidized coal is then removed and thoroughly washed and dried. Residual sulphuric acid in the wash water may be recovered and recycled in the process. After drying, the reaction product has the same appearance as the original coal and is of approximately the same or somewhat greater weight. The carbon content is now, however, only 50-60%. The loss in weight due to conversion of a part of the carbon to carbon dioxide has been made up, chiefly, by the addition of oxygen, and small amounts of sulphur.

To convert this primary oxidation product to the desired water soluble acids, 100 parts by weight of the primary product are mixed with approximately 350 parts potassium hydroxide

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and 600 parts of water. The whole is then subjected to the action of oxygen gas at 250° C. and total pressures of 750 p. s. i. in a pressure vessel equipped with internal agitator and suitable heating and cooling coils. After approximately 4 hours under these conditions, 40-50% of the carbon of the material charged has been converted to potassium carbonate and the balance to the potassium salts of organic acids. The free organic acids may be recovered by electrolysis of the salt solution or by acidification with a mineral acid, such as sulphuric, followed by extraction with an appropriate organic solvent, such as ethyl ether, isopropyl ether or methyl ethyl ketone. The mixture of acids recovered after distillation of the solvent amounts to about 40 parts per 100 parts by weight of the bituminous coal used in the primary stage.

Example 2

Place 1000 parts of dilute nitric acid, 2 N is a suitable concentration, in a glass-lined or stainless steel vessel equipped with reflux condenser and agitator. Add parts of -200 mesh bituminous coal and agitate at room temperature until the coal is thoroughly wet, then close the vessel and apply heat until steady reflux begins. Maintain this temperature for 24 hours. During the oxidation the nitric acid is reduced to nitric oxide which can be bled out of the reaction vessel, reconverted to dilute nitric acid by air oxidation and absorption in water and recycled in the process. At the close of this primary reaction period the oxidized coal is separated from the residual dilute nitric acid by filtration and is washed and dried. This primary oxidation product contains 55-60% carbon and is easily soluble in alkali, even at room temperatures. The yield is 80 to 90% of the weight of the coal used.

To convert this primary oxidation product to the desired water soluble acids, 100 parts by weight are mixed with 300 parts of sodium hydroxide and 600 parts of water. After agitation, the ash and any unattacked organic material remaining from the coal, such as fusain, may be separated from the alkaline solution by filtration and the oxidation of the alkaline solution of the primary oxidation product completed by the action of oxygen gas at 250° C. and 750 p. s. i. total pressure. For this purpose the alkaline solution of the primary oxidation product may be circulated continuously down a packed tower, counter-current to an ascending stream of oxygen gas, or it may be treated by batch operation in a pressure vessel fitted with suitable agitator and heating and cooling coils. In either case reaction is continued until 40-50% of the carbon of the primary oxidation product is converted to carbon dioxide. From the resulting solution of sodium carbonate and the sodium salts of the organic acids, the free organic acids are recovered in the same way as outlined under Example 1.

Example 3

One hundred parts by weight of finely divided coke are placed in a suitable lead-lined, horizontal, rotating reactor and, while being agitated, are subjected to the action of sulphur trioxide gas. The reactor is warmed by external heat until the temperature of the reaction mixture has reached 200° C. Due to the exothermic character of the reaction between sulphur trioxide and coke, this temperature can be maintained without the addition of external heat, simply by controlling the rate of input of the sulphur trioxide. The

reaction is continued until approximately 750 parts by weight of sulphur trioxide gas have been added. The exit gases contain carbon dioxide, sulphur dioxide and some sulphur trioxide. These gases may be separated by suitable methods and the sulphur dioxide, after re-oxidation, is recycled in the process. Fifteen to twenty per cent of the carbon of the coke appears as carbon dioxide in the exit gases. After the required amount of sulphur trioxide has been added, air is blown through the reactor to remove any residual sulphur trioxide and to cool the reactor to room temperature. The oxidized coke is then removed and thoroughly washed and dried. Residual sulphuric acid in the wash water may be recovered and recycled in the process. After drying, the reaction product has the same appearance as the original coke and is of approximately the same or somewhat greater weight. The carbon content is now, however, only 50-60%. The loss in weight due to conversion of a part of the carbon to carbon dioxide has been made up, chiefly, by the addition of oxygen, and small amounts of sulphur.

To convert this primary oxidation product to the desired water soluble acids, 100 parts by weight of the primary product are mixed with approximately 300 parts of sodium hydroxide and 600 parts of water. The whole is then subjected to the action of oxygen gas at 250° C. and total pressures of 750 p. s. i. in a pressure vessel equipped with internal agitator and suitable heating and cooling coils. After approximately 4 hours under these conditions, 40-50% of the carbon of the material charged has been converted to sodium carbonate and the balance to the sodium salts of organic acids. The free organic acids may be recovered by electrolysis of the salt solution or by acidification with a mineral acid, such as sulphuric, followed by extraction with an appropriate organic solvent, such as ethyl ether, isopropyl ether or methyl ethyl ketone. The mixture of acids recovered after distillation of the solvent amounts to about 47 parts per 100 parts by weight of the coke used in the primary stage.

Example 4

This example is identical with Example 3 except that pitch was used instead of coke and the yield of recovered acids was 60 parts instead of 47 parts.

Example 5

This example is identical with Example 3 except that carbon black was used instead of coke and the yield of recovered acids was 15 parts instead of 47 parts.

Example 6

Place 1000 parts of dilute nitric acid, 2 normal is a suitable concentration, in a glass-lined or stainless steel vessel equipped with reflux condenser and agitator. Add 100 parts of -200 mesh coke and agitate at room temperature until the coke is thoroughly wet, then close the vessel and apply heat until steady reflux begins. Maintain this temperature for 24 hours. During the oxidation the nitric acid is reduced to nitric oxide which can be bled out of the reaction vessel, reconverted to dilute nitric acid by air oxidation and absorption in water and recycled in the process. At the close of this primary reaction period the oxidized coke is separated from the residual dilute nitric acid by filtration and is washed and dried. This primary oxidation product contains

55-60% carbon and is easily soluble in alkali, even at room temperatures. The weight of oxidized product recovered is about the same as the weight of the coke charged.

To convert this primary oxidation product to the desired water soluble acids, 100 parts by weight are mixed with 300 parts of sodium hydroxide and 600 parts of water. After agitation, the ash and any unattacked organic material remaining from the coke may be separated from the alkaline solution by filtration and the oxidation of the alkaline solution of the primary oxidation product completed by the action of oxygen gas at 250° C. and 750 p. s. i. total pressure. For this purpose the alkaline solution of the primary oxidation product may be circulated continuously down a packed tower, counter-current to an ascending stream of oxygen gas, or it may be treated by batch operation in a pressure vessel fitted with suitable agitator and heating and cooling coils. In either case, reaction is continued until 40-50% of the carbon of the primary oxidation product is converted to carbon dioxide. From the resulting solution of sodium carbonate and the sodium salts of the organic acids, the free organic acids are recovered in the same way as outlined under Example 1.

Example 7

This example is identical with Example 6 except that pitch was used in place of coke.

Example 8

This example is identical with Example 6 except that carbon black was used in place of coke.

Example 9

Place 1000 ml. of 12 normal nitric acid in a glass-lined or stainless steel vessel, equipped with reflux condenser and agitator. Add 100 grams of carbon black and agitate at room temperature until the carbon black is thoroughly wet. Close the vessel and apply heat until steady reflux starts. Maintain this temperature for 24 hours. During the oxidation the nitric acid is reduced to nitric oxide which can be bled out of the reaction vessel, reconverted to nitric acid by air oxidation and absorption in water and recycled in the process. At the close of this primary oxidation period the nitric acid is distilled off and recovered. The residual non-volatile oxidation products are dark brown or black and resemble superficially the original carbon black. They are, however, readily soluble in alkali and electro-metric titration shows that they are a mixture of organic acids. About 40% of the carbon of the original samples is recovered as organic acids at this stage and the weight yield is about 65% of the original carbon black.

To convert this primary oxidation product to the desired water soluble acids, 100 parts by weight are mixed with 300 parts of sodium hydroxide and 600 parts of water. The oxidation of this alkaline solution of the primary oxidation product is completed and the organic acids recovered as described in Example 1. The yield of mixed, water soluble organic acids recovered is 30% by weight of the original carbon black. The acids recovered in this example are about one-fourth mellitic acid and three-fourths other water soluble aromatic acids.

I prefer to use relatively pure oxygen gas which is now commercially available and is inexpensive. However, air may be employed provided the pressure is such as to produce a partial pressure of

oxygen between 100 and 1000 lbs. per square inch.

The invention is not limited to the examples or to the preferred conditions which have been given merely for purposes of illustration, but may be otherwise embodied or practiced within the scope of the following claims.

I claim:

1. The process of making organic acids from carbonaceous material selected from the group consisting of coal, coke, carbon blacks and pitch, which comprises preoxidizing it by reacting it with an oxidizing agent which can be reoxidized by reaction with air at atmospheric pressure, dissolving the preoxidized material in an aqueous alkaline solution, treating the aqueous alkaline solution with oxygen gas at a temperature of 200° C. to 300° C. and at a partial pressure of oxygen of 100 to 1000 lbs. per square inch, recovering organic acids, reoxidizing the first mentioned oxidizing agent with air and recycling it in the process.

2. The process of making organic acids from carbonaceous material selected from the group consisting of coal, coke, carbon blacks and pitch, which comprises preoxidizing it by reacting it with an oxidizing agent selected from the group consisting of sulphur trioxide and nitric acid, dissolving the preoxidized material in an aqueous alkaline solution, treating the aqueous alkaline solution with oxygen gas at a temperature of 200° C. to 300° C. and at a partial pressure of oxygen of 100 to 1000 lbs. per square inch, recovering organic acids reoxidizing the first mentioned oxidizing agent with air and recycling it in the process.

3. The process of making organic acids from carbonaceous material selected from the group consisting of coal, coke, carbon blacks and pitch, which comprises preoxidizing it by reacting it with an oxidizing agent selected from the group consisting of sulphur trioxide and nitric acid, dissolving the preoxidized material in an aqueous alkaline solution of a concentration of 3 to 15 normal, treating the aqueous alkaline solution with oxygen gas at a temperature of 200° C. to 300° C. and at a partial pressure of oxygen of 100 to 1000 lbs. per square inch, recovering organic acids, reoxidizing the first mentioned oxidizing agent with air and recycling it in the process.

4. The process of making organic acids from coal, which comprises preoxidizing it by reacting it with sulphur trioxide, dissolving the preoxidized material in an aqueous alkaline solution, treating the aqueous alkaline solution with oxy-

gen gas at a temperature of 200° C. to 300° C. and at a partial pressure of oxygen of 100 to 1000 lbs. per square inch, recovering organic acids, reoxidizing sulphur dioxide to sulphur trioxide with air and recycling it in the process.

5. The process of making organic acids from coal, which comprises preoxidizing it by reacting it with sulphur trioxide, dissolving the preoxidized material in an aqueous alkaline solution of a concentration of 3 to 15 normal, treating the aqueous alkaline solution with oxygen gas at a temperature of 200° C. to 300° C. and at a partial pressure of oxygen of 100 to 1000 lbs. per square inch, recovering organic acids, reoxidizing sulphur dioxide to sulphur trioxide with air and recycling it in the process.

6. The process of making organic acids from coal, which comprises preoxidizing it by reacting it with nitric acid, dissolving the preoxidized material in an aqueous alkaline solution, treating the aqueous alkaline solution with oxygen gas at a temperature of 200° C. to 300° C. and at a partial pressure of oxygen of 100 to 1000 lbs. per square inch, recovering organic acids, reoxidizing nitric oxide to nitric acid with air and recycling it in the process.

7. The process of making organic acids from coal, which comprises preoxidizing it by reacting it with nitric acid, dissolving the preoxidized material in an aqueous alkaline solution of a concentration of 3 to 15 normal, treating the aqueous alkaline solution with oxygen gas at a temperature of 200° C. to 300° C. and at a partial pressure of oxygen of 100 to 1000 lbs. per square inch, recovering organic acids, reoxidizing nitric oxide to nitric acid with air and recycling it in the process.

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REFERENCES CITED

The following references are of record in the file of this patent:

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223,537	Switzerland	Dec. 1, 1942

Certificate of Correction

Patent No. 2,461,740.

February 15, 1949.

MYRON KIEBLER

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 1, line 38, for "bout" read *about*; column 4, line 24, Example 2, after "Add" insert the numeral *100*; column 8, line 47, list of references cited, for "Oct. 17, 1930" read *Oct. 17, 1939*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 21st day of June, A. D. 1949.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.