

PATENT SPECIFICATION

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International Classification:—C07b.

COMPLETE SPECIFICATION

Process for the Oxidation of Paraffins

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh 3, Scotland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improvements in a process for the production of C_1 — C_4 carboxylic acids, particularly acetic acid, by the liquid-phase oxidation with molecular oxygen paraffinic hydrocarbons containing 4—8 carbon atoms.

The liquid phase oxidation of low molecular weight paraffins to produce lower aliphatic acids is well known. Suitable feedstocks include C_4 to C_8 paraffins, obtained for example by the distillation of crude petroleum, and these are contacted with molecular oxygen at elevated temperatures and pressures in the presence or absence of added catalysts. The acids are suitably recovered from the oxidate by distillation. In one process, described in the British Patent Specification No. 743,990, the oxidate, or the aqueous phase from the oxidate, is distilled to separate the materials boiling in the presence of water below 99° C., hereinafter termed "light ends," before recovering the C_1 to C_4 acids from the oxidate, and the light ends are submitted to further oxidation, preferably with fresh hydrocarbon feed.

In the oxidation process as usually described, using air or oxygen-enriched air as oxidising agent, it is found that, owing to the high volatility of the hydrocarbons, appreciable quantities of hydrocarbons (accompanied by some low-boiling partial oxidation products, e.g., acetaldehyde) leave the apparatus in the stream of nitrogenous waste-gas from the oxidation even if this is cooled in conventional water-cooled condensers to about 30° C., and this results in a lower yield of acids per unit weight of hydrocarbon fed. It has

been proposed to remove this organic material from the waste-gas, for example by scrubbing the waste-gas (usually under pressure) with a high-boiling oil at atmospheric temperature in a suitable absorber. In order to recover this organic material, it must be then stripped from the oil with steam or by distillation, usually at a pressure lower than that used in the absorber. These recovered organic materials can then be recycled to the oxidation stage, where they are oxidised to give further yields of acids. Another method proposed for the recovery of these organic materials is to condense them by cooling the waste-gas to a sufficiently low temperature (below 0° C.) and then to recycle the condensate direct to the oxidation. It is found in practice, however, that cooling in this way leads to the separation of ice and/or other solid material which causes blockages in the cooling system and renders the operation of such a system technically difficult or impossible.

It is an object of the present invention to provide an improved process for the production of lower aliphatic carboxylic acids of 1 to 4 carbon atoms from paraffinic hydrocarbons. It is a further object of the invention to provide an improved process for the recovery of organic materials from the oxidation waste-gas, and the recycle of these to the oxidation stage whereby improved yields of the desired aliphatic acids are obtained.

According to the present invention the process for the production of lower aliphatic carboxylic acids, particularly acetic acid, comprises oxidising at elevated temperatures and pressures with a gas consisting of or comprising molecular oxygen a paraffin hydrocarbon of 4 to 8 carbon atoms or a mixture thereof in the liquid phase to produce lower aliphatic carboxylic acids of 1 to 4 carbon atoms, distilling the primary oxidation product to separate as light ends the materials boiling in the presence of water below 99° C., contacting

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at a temperature not above -1° C. the oxidation waste-gases with the light ends whereby organic materials from the waste gas are condensed, and thereafter oxidising the light ends together with the condensed material at an elevated temperature and pressure in the liquid phase with a gas consisting of or comprising molecular oxygen to produce additional quantities of lower aliphatic carboxylic acids of 1 to 4 carbon atoms.

In a preferred embodiment of the invention, the oxidation waste gases are first cooled to about 30° C. to condense out part of the volatile organic materials which are recycled to the oxidation stage, and the waste gases are then contacted with the light ends at a temperature not above -1° C., whereby further organic materials are condensed, the light ends with the condensed material then being subjected to further oxidation.

It has been discovered that, in the presence of these light ends, the degree of cooling required to ensure that substantially all of the organic materials are condensed, does not result in the deposition of ice or other solid material. The recovery is aided by working at or near the reaction pressure of the oxidation. The recovered organic material so obtained admixed with or in solution in light ends may be recycled directly to the main oxidation, or may be oxidised separately.

In order to obtain optimum recovery of the organic materials, the oxidation waste-gases are contacted with the light ends at a temperature between -1° and -50° C. It is preferred to use temperatures between -10° and -40° C. The cooling required may be produced by any known method, e.g., by heat exchanging with chilled brine or with a low-boiling refrigerant liquid, e.g., ammonia or methyl chloride. The light ends may be pre-cooled before contacting with the waste-gas, or the cooling may be applied to the contacting vessel, or both may be cooled. In our preferred method, the waste-gas, after removal of organic materials by the process of the invention, is expanded adiabatically, for instance in a heat engine, thereby furnishing, by means of suitable heat exchangers at least part of the cooling necessary for the process.

The process may be varied by cooling the waste-gas in the presence of light ends containing in solution filtered liquid residues (as defined below), the organic material so recovered being then recycled to the oxidation with the light ends and dissolved residues. These residues are the materials formed in the oxidation having boiling points above about 140° C. which have been subjected to filtration.

As starting material for the process it is preferred to use a paraffinic hydrocarbon fraction of a boiling range not exceeding about 100° C. As an example of a suitable starting material may be mentioned a C_4 to C_6

paraffinic hydrocarbon fraction boiling between about 15° and 95° C. derived from petroleum.

The process of the invention is further illustrated by the following example:

EXAMPLE.

The oxidation reactor and its ancillary equipment are shown diagrammatically in the accompanying drawing in which the reactor (1) has two air feed points (2) at the base and about the mid-point. Fresh hydrocarbon was introduced continuously by line (3) via pump (4). The reactor was run full, and a mixture of gaseous and liquid reaction products passed out from the reactor by line (5). The liquid products were separated in a separator (6) and returned directly to the bottom of the oxidation tower by line (7). The hot vapour/waste-gas mixture from the separator (6) was cooled in a cooler (8), and the liquid condensate separated in the separator (9), and fed back into the main liquid recycle via preheater (10). Aqueous reaction product was continuously withdrawn from the system via the cooled separator (11), and reduced to atmospheric pressure through the valve (12). Any separated hydrocarbon layer from the separator (11), returned to the reactor with the rest of the liquid recycle via line (7). The aqueous product from (11) was fed to a continuous still (13) where the light ends were taken off at the head and passed to an intermediate storage vessel (14), the kettle product consisting of acids, water and residues. The kettle product from the still (13) was passed to a second continuous still (21), where the C_1 — C_4 acids and water were taken off at the head through line (22) to a storage vessel (23), and the residues were taken off from the kettle through line (24). The formic, acetic, propionic and butyric acids were recovered from the product in (23) by fractional distillations. The residues were cooled to below 30° and filtered (25) from the separated solid (largely succinic acid). The liquid residues from (25) were then pumped back to the oxidation, but for part of the run this was done by feeding to the storage vessel (14) via line (26) and mixing with the light ends.

The waste-gas containing organic material, still under reaction pressure, passed from the separator (9) through line (20) into the base of a jacketed packed tower (17) situated at a height several feet above the oxidation tower, and cooled to about -18° C. The light ends from storage (14) were transferred by pump (15) to a cooler (16) under the reaction pressure, where they were cooled to an average temperature of -18° C. and then passed to the top of tower (17). In the tower (17) the waste-gas was brought into intimate contact with the cooled light ends. The waste-gas from which most of the organics had been removed passed out of the top (17), and was vented to atmosphere through valve (18). The solution of recovered organic material in light ends

returned by gravity to the reaction system by line (19), joining in with the major liquid recycle and hydrocarbon feed to the reactor.

The feed to the oxidation was a cut from a Middle East petroleum, with a boiling range of approximately 30—70° C., and consisting mainly of paraffinic hydrocarbons. The oxidation was carried out in the liquid phase at a temperature of 175° C. and at 630 lbs./sq. inch, with air as the oxidising agent; no catalyst was added. The waste-gas from the oxidation contained 0—5% oxygen.

A continuous oxidation carried out in this way for a total period of 196 hours gave the following yields of acids, expressed as parts by weight per 100 parts by weight of fresh hydrocarbon fed through line (3); formic acid 14.6, acetic acid 67.5 propionic acid 9.5, butyric acid 1.65; total 93.25 parts.

By way of comparison with the above Example, when the corresponding process was carried out, with recycle of both light ends and residues to the oxidation, but with the waste-gas from separator (9) vented to atmosphere without treating in accordance with this invention, the yield of acids obtained was much reduced, being as follows: formic acid 11.3, acetic acid 48.1, propionic acid 2.8, butyric acid 0.7; total 62.9 parts per 100 parts of hydrocarbon fed.

WHAT WE CLAIM IS:—

1. The process for the production of lower aliphatic carboxylic acids which comprises oxidising at elevated temperatures and pressures with a gas consisting of or comprising molecular oxygen a paraffin hydrocarbon of 4 to 8 carbon atoms or a mixture thereof in the liquid phase to produce lower aliphatic carboxylic acids of 1 to 4 carbon atoms, distilling the primary oxidation product to separate as light ends the materials boiling in the presence of water below 99° C., contacting at a temperature not above -1° C., the oxidation waste gases with the light ends whereby organic materials from the waste gases are condensed, and thereafter oxidising the light ends together with the condensed material at an elevated temperature and pressure in the liquid phase with a gas consisting of or comprising molecular oxygen to produce additional quantities of

lower aliphatic carboxylic acids of 1 to 4 carbon atoms.

2. The process as claimed in claim 1 wherein the oxidation waste gases are cooled to about 30° C. to condense out part of the volatile organic materials, said part being recycled to the oxidation stage, before being contacted with the light ends at a low temperature.

3. The process as claimed in any of the preceding claims wherein the oxidation waste gases are contacted with the light ends at a temperature between -1° and -50° C.

4. The process as claimed in any of the preceding claims wherein the oxidation waste gases are contacted with the light ends at a temperature between 10° and -40° C.

5. The process as claimed in any of the preceding claims wherein the light ends containing condensed material from the oxidation waste gases are recycled to the oxidation stage.

6. The process as claimed in any of the preceding claims wherein the oxidation waste gases are contacted with the light ends at the pressure used in the oxidation reaction.

7. The process as claimed in claim 6 wherein the waste gas after being contacted with the light ends is expanded adiabatically to furnish at least part of the cooling necessary for the process.

8. The process as claimed in any of the preceding claims wherein the oxidation waste gases are contacted with light ends containing in solution, filtered, liquid oxidation residues as hereinbefore defined.

9. The process for the production of lower aliphatic carboxylic acids of 1 to 4 carbon atoms according to any of the preceding claims substantially as hereinbefore described in the examples.

10. The process for the production of lower aliphatic carboxylic acids of 1 to 4 carbon atoms substantially as hereinbefore described with reference to the accompanying drawing.

11. Lower aliphatic carboxylic acids of 1 to 4 carbon atoms when produced by the process of any of the preceding claims.

N. F. BAKER,

Agent for the Applicants.

PROVISIONAL SPECIFICATION

Process for the Oxidation of Paraffins

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh 3, Scotland, do hereby declare this invention to be described in the following statement:—

This invention relates to improvements in a process for the production of C₁—C₄ acids, particularly acetic acid by the liquid-phase oxidation with molecular oxygen of substan-

tially paraffinic hydrocarbons containing 4—8 carbon atoms.

The liquid phase oxidation of low molecular weight paraffins to produce lower aliphatic acids is well known. Suitable feedstocks include C₄ to C₈ paraffins, obtained for example by the distillation of crude petroleum, and these are contacted with molecular oxygen at elevated temperatures and pressures



returned by gravity to the reaction system by line (19), joining in with the major liquid recycle and hydrocarbon feed to the reactor.

5 The feed to the oxidation was a cut from a Middle East petroleum, with a boiling range of approximately 30–70° C., and consisting mainly of paraffinic hydrocarbons. The oxidation was carried out in the liquid phase at a temperature of 175° C. and at 630
10 lbs./sq. inch, with air as the oxidising agent; no catalyst was added. The waste-gas from the oxidation contained 0–5% oxygen.

A continuous oxidation carried out in this way for a total period of 196 hours gave the
15 following yields of acids, expressed as parts by weight per 100 parts by weight of fresh hydrocarbon fed through line (3); formic acid 14.6, acetic acid 67.5 propionic acid 9.5, butyric acid 1.65; total 93.25 parts.

20 By way of comparison with the above Example, when the corresponding process was carried out, with recycle of both light ends and residues to the oxidation, but with the waste-gas from separator (9) vented to
25 atmosphere without treating in accordance with this invention, the yield of acids obtained was much reduced, being as follows: formic acid 11.3, acetic acid 48.1, propionic acid 2.8, butyric acid 0.7; total 62.9 parts per 100 parts
30 of hydrocarbon fed.

WHAT WE CLAIM IS:—

1. The process for the production of lower aliphatic carboxylic acids which comprises oxidising at elevated temperatures and
35 pressures with a gas consisting of or comprising molecular oxygen a paraffin hydrocarbon of 4 to 8 carbon atoms or a mixture thereof in the liquid phase to produce lower aliphatic carboxylic acids of 1 to 4 carbon
40 atoms, distilling the primary oxidation product to separate as light ends the materials boiling in the presence of water below 99° C., contacting at a temperature not above –1° C., the oxidation waste gases with the light
45 ends whereby organic materials from the waste gases are condensed, and thereafter oxidising the light ends together with the condensed material at an elevated temperature and pressure in the liquid phase with a
50 gas consisting of or comprising molecular oxygen to produce additional quantities of

lower aliphatic carboxylic acids of 1 to 4 carbon atoms.

2. The process as claimed in claim 1 wherein the oxidation waste gases are cooled
55 to about 30° C. to condense out part of the volatile organic materials, said part being recycled to the oxidation stage, before being contacted with the light ends at a low temperature.
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3. The process as claimed in any of the preceding claims wherein the oxidation waste gases are contacted with the light ends at a temperature between –1° and –50° C.

4. The process as claimed in any of the preceding claims wherein the oxidation waste gases are contacted with the light ends at a temperature between –10° and –40° C.
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5. The process as claimed in any of the preceding claims wherein the light ends containing condensed material from the oxidation waste gases are recycled to the oxidation stage.
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6. The process as claimed in any of the preceding claims wherein the oxidation waste gases are contacted with the light ends at the pressure used in the oxidation reaction.
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7. The process as claimed in claim 6 wherein the waste gas after being contacted with the light ends is expanded adiabatically to furnish at least part of the cooling necessary for the process.
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8. The process as claimed in any of the preceding claims wherein the oxidation waste gases are contacted with light ends containing in solution, filtered, liquid oxidation residues as hereinbefore defined.
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9. The process for the production of lower aliphatic carboxylic acids of 1 to 4 carbon atoms according to any of the preceding claims substantially as hereinbefore described in the examples.
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10. The process for the production of lower aliphatic carboxylic acids of 1 to 4 carbon atoms substantially as hereinbefore described with reference to the accompanying drawing.
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11. Lower aliphatic carboxylic acids of 1 to 4 carbon atoms when produced by the process of any of the preceding claims.
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R.H.

PROVISIONAL SPECIFICATION

Process for the Oxidation of Paraffins

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh 3, Scotland, do hereby declare
105 this invention to be described in the following statement:—

This invention relates to improvements in a process for the production of C₁–C₄ acids, particularly acetic acid by the liquid-phase oxidation with molecular oxygen of substan-

tially paraffinic hydrocarbons containing 4–8
110 carbon atoms.

The liquid phase oxidation of low molecular weight paraffins to produce lower aliphatic acids is well known. Suitable feedstocks include C₄ to C₈ paraffins, obtained for
115 example by the distillation of crude petroleum, and these are contacted with molecular oxygen at elevated temperatures and pressures

in the presence or absence of adding catalysts. The acids are suitably recovered from the oxidate by distillation. In one process, described in our Patent Specification No. 743,990, the oxidate, or the aqueous phase from the oxidate, is distilled to separate the materials boiling up to 99° C. in the presence of water, hereinafter termed "light ends," before recovering the C₁ to C₄ acids from the oxidate, and the light ends are submitted to further oxidation, preferably with fresh hydrocarbon feed.

In the oxidation process as usually described, using air or oxygen-enriched air as oxidising agent, it is found that, owing to the high volatility of the hydrocarbons, appreciable quantities of hydrocarbons (accompanied by some low-boiling partial oxidation products, e.g., acetaldehyde) leave the apparatus in the stream of nitrogenous waste-gas from the oxidation even if this is cooled in conventional water-cooled condensers to about 30° C., and this results in a lower yield of acids per unit weight of hydrocarbon fed. This organic material can be removed from the waste-gas to a large extent by known methods, for example by scrubbing the waste-gas (usually under pressure) with a high-boiling oil at atmospheric temperature in a suitable absorber. In order to recover this organic material, it must then be stripped from the oil with steam or by distillation, usually at a pressure lower than that used in the absorber. These recovered organic materials can then be recycled to the oxidation stage, where they are oxidised to give further yields of acids. Another method for the recovery of these organic materials is to condense them by cooling the waste-gas to a sufficiently low temperature (below 0° C.) and then to recycle the condensate direct to the oxidation. It is found in practice, however, that cooling in this way leads to the separation of ice and/or other solid material which causes blockages in the cooling system and renders the operation of such a system technically difficult or impossible.

It is an object of the present invention to provide an improved process for the production of lower aliphatic acids from paraffinic hydrocarbons. It is a further object of the invention to provide an improved process for the recovery of organic materials from the oxidation waste-gas, and the recycle of these to the oxidation stage whereby improved yields of the desired aliphatic acids are obtained.

According to the present invention, the process for the production of lower aliphatic acids, particularly acetic acid, comprises oxidising at an elevated temperature in the liquid phase with molecular oxygen a paraffin hydrocarbon of 4 to 8 carbon atoms or a mixture thereof to produce lower aliphatic acids of 1 to 4 carbon atoms, distilling the

primary oxidation product to separate as light ends the materials boiling below 99° C. in the presence of water, contacting at a low temperature the oxidation waste-gases with the light ends whereby organic materials from the waste gas are condensed, and thereafter oxidising the light ends with the condensed material at an elevated temperature in the liquid phase with molecular oxygen to produce lower aliphatic acids.

In a preferred embodiment of the invention, the oxidation waste gases are first cooled to about 30° C. to condense out part of the volatile organic materials which are recycled to the oxidation stage, and the waste gases are then contacted with the light ends at a low temperature whereby further organic materials are condensed, the light ends with the condensed material then being subjected to further oxidation.

It has been discovered that, in the presence of these light ends, the degree of cooling required to ensure that substantially all of the organic materials are condensed, does not result in the deposition of ice or other solid material. The recovery is aided by working at or near the reaction pressure of the oxidation. The recovered organic material so obtained admixed with or in solution in light ends may be recycled directly to the main oxidation, or may be oxidised separately.

In order to obtain optimum recovery of the organic materials, the waste-gas is cooled to -1° to -50° C. in contact with the light ends. We prefer to work in the range -10° to -40° C. The cooling required may be produced by any known method, e.g. by heat exchanging with chilled brine or with a low-boiling refrigerant liquid, e.g. ammonia or methyl chloride. The light ends may be pre-cooled before contacting with the waste-gas, or the cooling may be applied to the contacting vessel, or both may be cooled. In our preferred method, the waste-gas, after removal of organic materials by the process of the invention, is expanded adiabatically, thereby furnishing, by means of suitable heat exchangers, the cooling necessary for the process.

The process may be varied by cooling the waste-gas in the presence of light ends containing dissolved filtered liquid residues (as defined below), the organic material so recovered being then recycled to the oxidation with the light ends and dissolved residues. These residues are the materials formed in the oxidation having boiling points above about 140° C.

The process of the invention is further illustrated by the following example:

EXAMPLE.

The oxidation reactor and its ancillary equipment are shown diagrammatically in the accompanying drawing in which the reactor (1) has two air feed points (2) at the base and

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about the mid-point. Fresh hydrocarbon was introduced continuously by line (3) via pump (4). The reactor was run full, and a mixture of gaseous and liquid reaction products passed out from the reactor by line (5). The liquid products were separated in a separator (6) and returned directly to the bottom of the oxidation tower by line (7). The hot water vapour/water-gas mixture from the separator (6) was cooled in a cooler (8), and the liquid condensate separated in the separator (9), and fed back into the main liquid recycle via pre-heater (10). Aqueous reaction product was continuously withdrawn from the system via the cooled separator (11), and reduced to atmospheric pressure through the valve (12). Any separated hydrocarbon layer from the separator (11) returned to the reactor with the rest of the liquid recycle via line (7). The aqueous product from (11) was fed to a continuous still (13) where the light ends were taken off at the head and passed to an intermediate storage vessel (14), the kettle product consisting of acids, water and residues. The kettle product from the still (13) was passed to a second continuous still (21), where the C_1 — C_4 acids and water were taken off at the head through line (22) to a storage vessel (23), and the residues were taken off from the kettle through line (24). The formic, acetic, propionic and butyric acids were recovered from the product in (23) by fractional distillations. The residues were cooled to below 30° and filtered (25) from the separated solid (largely succinic acid). The liquid residues from (25) were then pumped back to the oxidation, but for part of the run this was done by feeding to the storage vessel (14) via line (26) and mixing with the light ends.

The waste-gas containing organic material, still under reaction pressure, passed from the separator (9) through line (20) into the base of a jacketed packed tower (17) situated at a height several feet above the oxidation tower,

and cooled to about -18°C . The light ends from storage (14) were transferred by pump (15) to a cooler (16), where they were cooled to an average temperature of -18°C , and then passed to the top of tower (17). In the tower (17) the waste-gas was brought into intimate contact with the cooled light ends. The waste-gas from which most of the organics had been removed passed out of the top (17), and was vented to atmosphere through valve (18). The solution of recovered organic material in light ends, returned by gravity to the reaction system by line (19), joining in with the major liquid recycle and hydrocarbon feed to the reactor.

The feed to the oxidation was a cut from a Middle East petroleum, with a boiling range of approximately 30 — 70°C ., and consisting mainly of paraffinic hydrocarbons. The oxidation was carried out at a temperature of 175°C . and at 630 lbs./sq. inch, with air as the oxidising agent; no catalyst was added. The waste-gas from the oxidation contained 0—5% oxygen.

A continuous oxidation carried out in this way for a total period of 196 hours gave the following yields of acids, expressed as parts by weight per 100 parts by weight of fresh hydrocarbon fed through line (3); formic acid 14.6, acetic acid 67.5, propionic acid 9.5, butyric acid 1.65; total 93.25 parts.

By way of comparison with the above Example, when the corresponding process was carried out, with recycle of both light ends and residues to the oxidation, but with the waste-gas from separator (9) vented to atmosphere without treating in accordance with this invention, the yield of acids obtained was much reduced, being as follows: formic acid 11.3, acetic acid 48.1, propionic acid 2.8, butyric acid 0.7; total 62.9 parts of hydrocarbon fed.

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