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PROCESS FOR THE PRODUCTION OF DICARBOXYLIC ACIDS

Filed Feb. 10, 1965

3 Sheets-Sheet 2

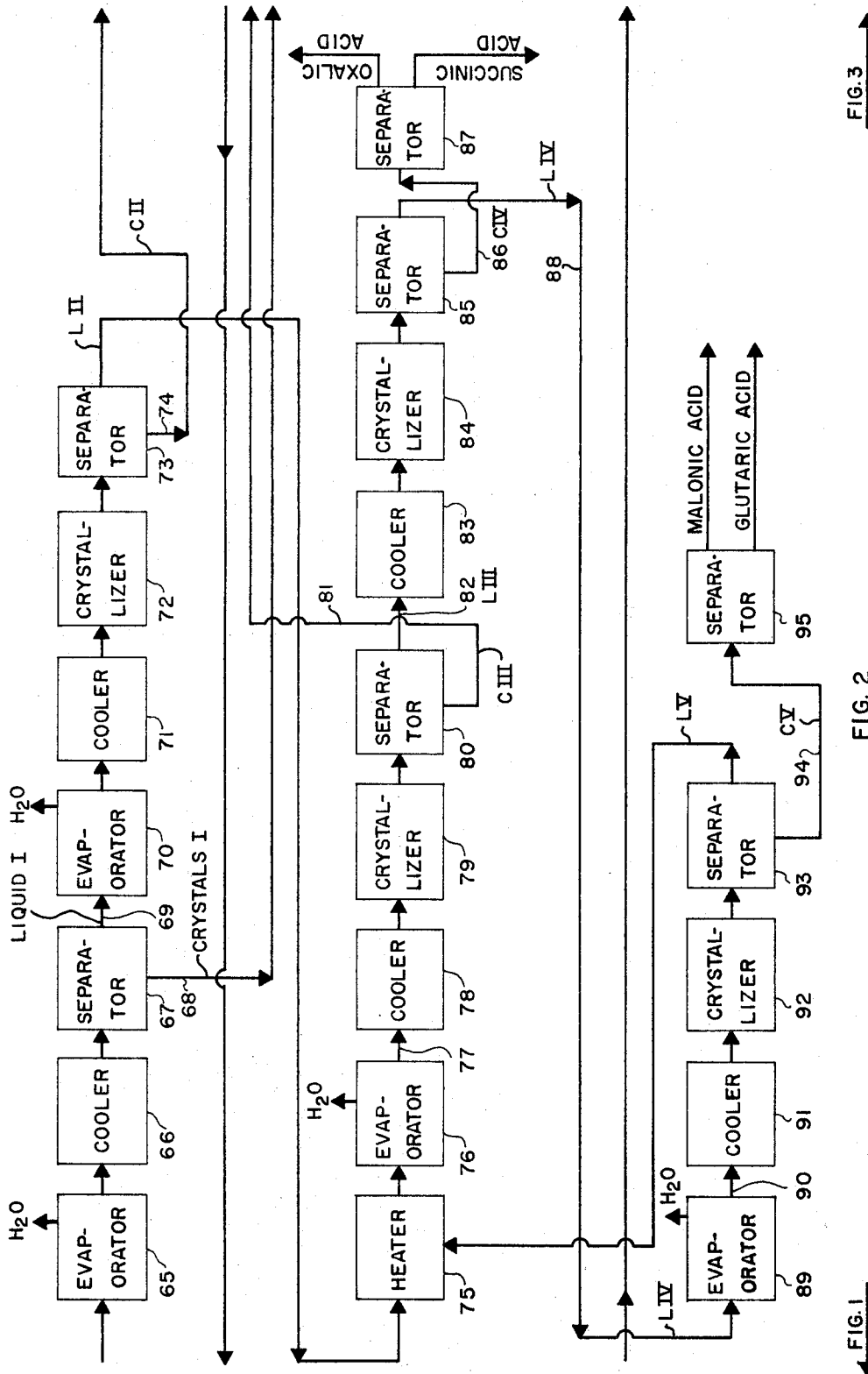


FIG. 3

FIG. 2

FIG. 1

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3 Sheets-Sheet 3

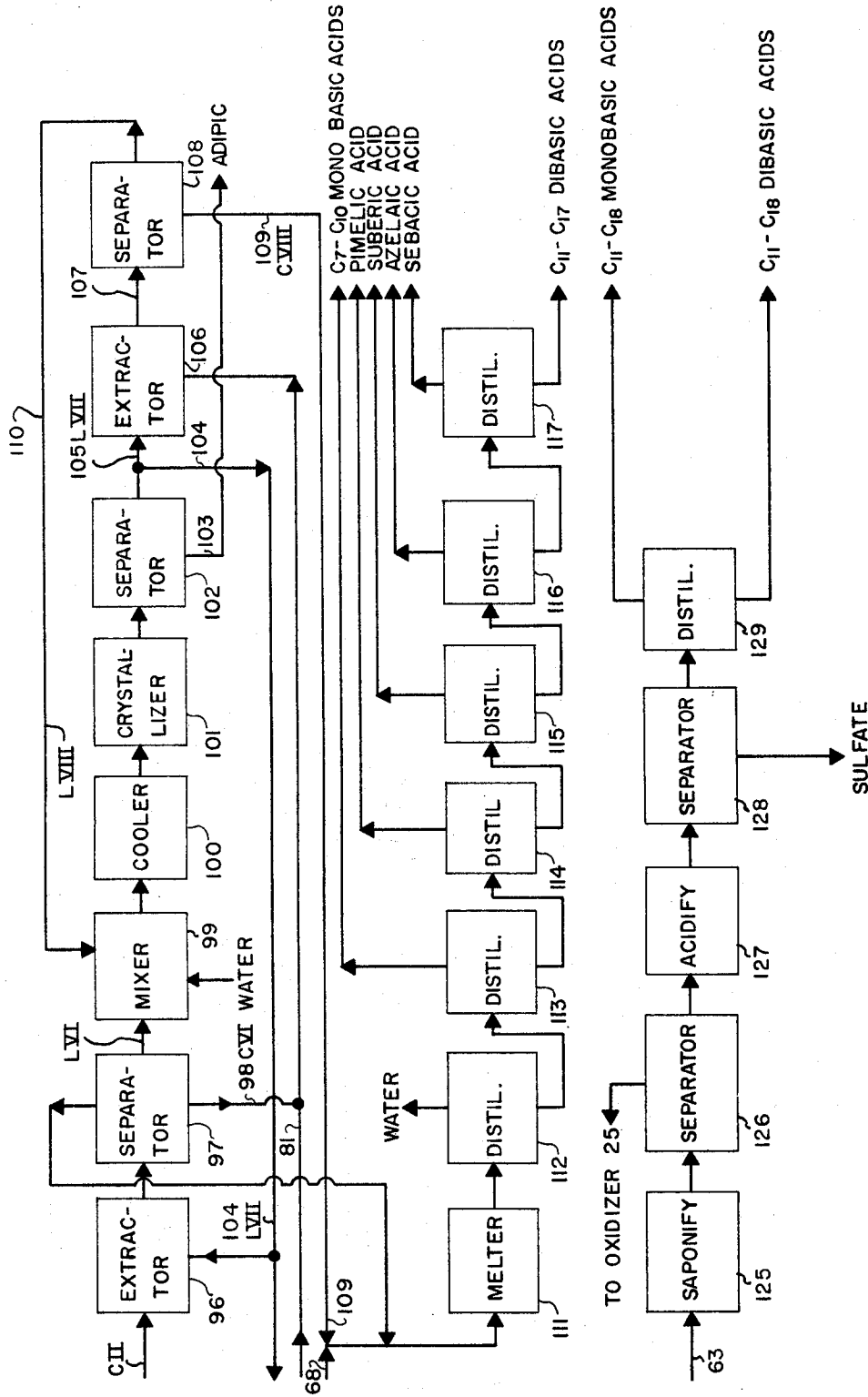


FIG. 2

FIG. 3

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PROCESS FOR THE PRODUCTION OF
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ABSTRACT OF THE DISCLOSURE

Process is disclosed where hydrocarbons are partially oxidized, hydrogenated to convert the non-acid oxygenated molecules to paraffins, the product being then separated into light and heavy fractions. The light fraction is extracted with water and heavy paraffin to recover light acids. The heavy fraction is extracted with water to separate in a water phase the water soluble dicarboxylic acids and some intermediate monocarboxylic acids. The extracted acids are then separated into virtually individual acids in high yield.

This invention relates to the production of carboxylic acids by the oxidation of hydrocarbons and in particular to the recovery of dicarboxylic acids produced by the oxidation of hydrocarbons.

An object of this invention is to provide a practical commercial process for the recovery of the members of the dicarboxylic acid homologous series from a mixture thereof, said acids having a typical range of chain length from two to eighteen carbon atoms but not restricted to this range.

Another object of the present invention is to provide a process whereby dicarboxylic acids are withdrawn from the oxidate from a hydrocarbon oxidation prior to saponification to avoid the requirement for raw material expense in saponification and in acidification of dicarboxylic acids.

Other and further objects and features of the present invention will become apparent upon a careful consideration of the following detailed description and accompanying drawings which illustrate a preferred embodiment of the features of the present invention, wherein,

FIGS. 1, 2 and 3 show various portions of an overall process, with coordination between the figures being indicated.

In accordance with the basic teachings of the present invention, an improved process for the production of carboxylic acids by the oxidation of hydrocarbons is provided in which the oxidate is hydrogenated to convert the contents thereof to acids and paraffins following which the material is divided into a light fraction and a heavy fraction, the former being extracted with water and heavy paraffin for the recovery of light acids and the latter being extracted with water to separate in a water phase the water soluble dicarboxylic acids and some intermediate monocarboxylic acids not removed as a part of the light fraction. The extracted acids are then subjected to a unique combination of evaporation, crystallization and recrystallization followed by distillation whereby the dicarboxylic acids are recovered on virtually an individual basis in high yield and with small losses.

With reference now to the drawing, a preferred embodiment of the features of the invention is shown which for clarity is contained in an expanded presentation covering several sheets keyed together. Each sheet is indicated by a separate figure for ease of reference, however it is to be understood that all of these together constitute a complete coordinated process.

With particular reference to FIG. 1 of the drawing, a

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hydrocarbon feed such as a mixture of straight chain alkanes having from 12–20 carbon atoms per molecule is supplied to oxidizer system 25 wherein air oxidation is conducted at a temperature from about 100 to about 250° C., typically 160° C. Catalysts may be employed such as organic peroxides, or various inorganic materials, such as manganese carboxylate or a peroxide-containing heel from a previous run. Oxidation may continue over a period of several hours with a vent and recovery system 26 being provided to remove materials from the off-gases and collect desired materials for utilization either in the present process or elsewhere. Some of the lower monocarboxylic acids can be removed in this way if desired.

The oxidizer system preferably includes a hydrogenation stage or other suitable purification arrangement whereby incompletely oxidized materials as well as over-oxygenated materials may be converted into carboxylic acids or saturated hydrocarbon, the latter being removed for internal recycle to the oxidizer or allowed to remain for separation as with external apparatus herein typified.

Thus the oxidate from the oxidizer system 25 of FIG. 1 will contain unreacted feed hydrocarbon, monocarboxylic acids and dicarboxylic acids.

This oxidate stream is fed to distillation 50 in which is accomplished a separation of the material into a light fraction and a heavy fraction. Distillation 50 involves the usual complement of condenser, reflux and reboiler components which are of a more or less conventional nature. The overhead or light fraction from distillation 50 is supplied to a mixer 51, where it is agitated with water, the water soluble components of the light fraction dissolving in the water. The mixed stream is delivered to a phase separator 52 wherein separation into hydrocarbon and aqueous phases occurs. The hydrocarbon phase consists essentially of light paraffins and other non-water soluble materials and is withdrawn through line 53 and recycled to oxidizer system 25. The aqueous phase withdrawn from phase separator 52 through line 54 contains principally the lower monocarboxylic acids. These lower acids are extracted with hydrocarbon such as a mixture of C₁₄–C₁₇ straight chain alkanes in mixer 55 provided for this purpose. The output from the mixer is fed to phase separator 56 which separates aqueous and hydrocarbon phases, the aqueous phase being withdrawn through line 57 and typically returned to mixer 51 as a recycle water stream for the water extraction of the light fraction.

The hydrocarbon phase obtained from phase separator 56 contains the lower acids and heavy hydrocarbon extractant, and a relatively small amount of water. This hydrocarbon phase is delivered through line 58 to a hydrocarbon recovery device such as distillation 59 from which the acids are withdrawn as overhead and the heavy paraffin bottoms contained in line 60 are withdrawn and returned to mixer 55 for recycle, makeup hydrocarbon being provided as required.

An important feature of the extraction of the lower acids with heavy n-alkanes as thus far described is that the lower monocarboxylic acids which are normally soluble in water are separated from most of the water by the paraffin extraction. This operation makes economically feasible, and in the case of highly diluted aqueous solutions of light acids, makes possible the recovery of these acids by azeotropic and/or extractive distillation. This feature is an important part of the economic operation of this process.

The heavy fraction obtained as bottoms from distillation 50 is cooled and then delivered to mixer 61 wherein water or a dilute water-acid solution is comingled therewith to accomplish extraction of the water soluble constituents of the fraction. The aqueous and non-aqueous phases are separated in phase separator 62. The non-

aqueous phase consists principally of monocarboxylic acids having from about 7 to about 18 carbon atoms per molecule, dicarboxylic acids having from about 11 to about 18 carbon atoms per molecule and normal paraffins having from about 13-18 carbon atoms per molecule. This phase is delivered to saponifier 125 of FIG. 3. The aqueous phase from phase separator 62 contains in addition to water, intermediate monocarboxylic acids having from about 7 to about 10 carbon atoms per molecule and dicarboxylic acids up to about 10 carbon atoms per molecule. This mixture is processed according to the scheme shown in FIG. 2 in which oxalic, malonic, succinic, glutaric, and adipic acids are recovered by a combination of successive evaporations, crystallizations at carefully controlled temperatures, crystal separations, and recrystallization. From the residue of these operations, higher acids, such as pimelic, suberic, azelaic, and sebacic acids are recovered and separated by distillation.

With particular reference now to FIG. 2 of the drawing, a first evaporator 65 concentrates the acids to provide a supersaturated solution of pimelic, suberic, azelaic, and sebacic acids at a temperature in the region of 85-110° C., such as 100° C. Crystals (crystals I) thus formed are removed from their mother liquor in crystal separator 67 which as subsequent separators typically is a centrifuge, filter press, or other suitable separation device, the crystals being delivered to line 68 and the liquor I being withdrawn through line 69. Cooler 66 is provided to lower the temperature of the effluent from separator 65 so that it is below its boiling point at atmospheric pressure but not below about 85° C. and preferably is near 100° C., which provides the desired solubility ratios for the separation sought at this point.

Liquor I is then delivered to evaporator 70 where additional water is removed. The solution is cooled (cooler 71) to a temperature in the region of 45° to 85° C., typically 60° C., where adipic acid is only slightly soluble and, in crystallizer 72, separates out leaving oxalic, malonic, succinic and glutaric acids in the mother liquor (liquor II). The crystals (crystals II) are separated from the liquor by a suitable separator 73. Crystals thus obtained are delivered to a suitable conveyor system 74 and are treated in subsequent purification which will be described later.

Mother liquor II still contains some adipic and higher acids, however, because the separation is not complete, and a satisfactory purity of the oxalic, malonic, succinic and glutaric acids requires succedent evaporation, crystallization and separation.

To this end, the mother liquor (II) from separator 73 is preheated (heater 75) and delivered to a third evaporator 76 where further concentration occurs. The concentrate withdrawn therefrom (line 77) is cooled (cooler 78) again to a temperature in the region of 45° to 85° C., typically 60° C., and delivered to crystallizer 79 which is maintained at 60° C. This temperature may be the same as that of the crystallization 72, or it can be different as long as it is in the specified region. On the other hand, conducting both crystallizations at about 60° C. is preferable since it provides an excellent combination of rapid crystallization rate and a high degree of separation.

Materials from crystallizer 79 are delivered to separator 80 from which crystals III and liquor III are obtained.

Liquor III is a mixture of oxalic, malonic, succinic, and glutaric acids but now with mere traces of adipic acid. Separation of the oxalic and succinic acids is accomplished by cooling the liquor III (cooler 83) to a temperature in the region of 0-45° C., typically 15° C., where oxalic and succinic acids are only slightly soluble and, in crystallizer 84 separate out. Separator 85 provides crystals IV in line 86 and malonic and glutaric acids in solution in line 88 as mother liquor IV. Liquor IV contains traces of adipic acid and significant quantities of oxalic and succinic acid. Crystals IV in line 86 are primarily mixed oxalic and succinic acids which are separated as by a

suitable organic solvent extraction and recovery system indicated in general by the reference character 87.

As mentioned liquor IV contains principally malonic and glutaric acids but significant quantities of oxalic and succinic acids and traces of adipic acid. This is delivered to a fourth evaporator 89 where additional water is removed by boiling at atmospheric pressure or under vacuum, as desired. The concentrate contained in line 90 is then cooled (cooler 91) to a temperature in the region of 0-45° C., typically 15° C., and is delivered to crystallizer 92. The crystals (V) that form are quite pure malonic and glutaric acids from which the mother liquor V is removed by separator 93. Crystallization of the impurities oxalic, succinic, and adipic does not occur because the concentration is too low. As with oxalic and succinic acids, malonic and glutaric acids are separated by a suitable solvent extraction and recovery system 95.

Liquor V contains a mixture of adipic, pimelic, and higher acids which is subjected to further separation treatment by way of recycle through the adipic, oxalic and succinic separation stages being returned to heater 75 where it is combined with liquor II.

The crystals II from conveyor system 74 are slurried in extractor 96 (FIG. 3) with liquor VII (line 104) derived from a portion of the process not yet discussed but which will be explained presently. The slurring operation takes place at approximately 100° C. The crystals II become involved in what may be described as concurrent melting and recrystallization following which new crystals VI are produced which are recovered by separator 97 and delivered to line 98. Resultant liquor VI contains a mixture of adipic, pimelic and higher acids and is combined in mixer 99 with liquor VIII (line 110) and with additional water. The mixture is cooled (cooler 100) to a temperature in the region of 80-100° C., typically 90° C., following which the material is delivered to a crystallizer 101. Crystals produced here are almost pure adipic acid and are recovered by a separator 102 which as with previous separators is typically a centrifuge or filter press device. Adipic acid crystals thus recovered are delivered in line 103 as a product acid. Separator 97 is also a decanter arrangement wherein intermediate monocarboxylic acids having from about 7 to about 10 carbon atoms are neither crystals nor are they water soluble. These are withdrawn as a separate liquid phase and are delivered to melter 111 as will be described subsequently. Actually the quantity of these acids is small and separation of intermediate acids is not complete since some of them will remain occluded on crystals VI and subsequently on crystals VIII.

The liquor obtained from separator 102 is identified as liquor VII and contains residual adipic acid mixed with small amounts of pimelic and higher acids. This is split, part returning to extractor 96 through line 104 for mingling with crystals II as previously mentioned and another part passing through line 105 to extractor 106. Provision for handling some of this return dilute material as by delivery to the mixer 61 (FIG. 1) to smooth out peaks and upsets is shown. Normally in uniform operation the quantity of material thus returned is small in proportion to the other materials going to mixer 61 but may be approximately half of the output of separator 102. Extractor 106 also receives the crystals III from separator 80 and crystals VI from separator 97, again these crystals become involved in a process that may be described as concurrent melting and recrystallization. The resulting mixture is delivered through line 107 to separator 108 which recovers the crystals VIII for delivery to line 109 and liquor VIII which is delivered through line 110 to mixer 99 for recycle processing. Liquor VIII is a mixture of adipic, pimelic and higher acids.

Liquors V, VI, VII and VIII contain generally similar materials, namely adipic, pimelic and higher acids, however the ratios of these materials and the water content of the various streams, is different. The efficient utilization

of these streams is an important feature of the present invention.

Crystals I from separator 67, and crystals VIII from separator 108, both being largely pimelic and higher dibasic acids, together with intermediate monocarboxylic acids from separator 97 are transferred to a melter 111, at which point they are heated to a suitable temperature such as approximately 120° C., to convert all to liquid, but which is not sufficiently high to cause serious degradation of the acids. In this connection it is observed that the crystals at this point contain a substantial amount of water and some liquid acids which are not water soluble. The water is stripped in a first distillation 112 as an overhead stream which can be discarded or returned to the process whichever may be preferred.

Acid bottoms from stripper 112 are transferred to distillation column 113 which preferably operates under reduced pressure of the order of 5 to 400 mms. Hg, typically 50 mms. Hg. The temperature at the bottom of the distillation column 113 is in the region from about 160 to about 190° C., typically of the order of 175° C. Overhead recovered from distillation column 113 is made up primarily of mid-range monocarboxylic acids having from about 7 to about 10 carbon atoms per molecule which are taken off as a product cut.

The bottoms stream of distillation column 113 in turn passes to distillation column 114 which again is a vacuum distillation device having a typical bottoms temperature of 290° C. and an overhead temperature of the order of 250° C. The overhead of this distillation column 114 is principally pimelic acid which is taken off a product acid stream.

In turn the bottoms of distillation column 114 passes to distillation column 115 which operates in a similar manner to provide as overhead suberic acid which is again a product acid stream.

In turn the distillation columns 116 and 117 provide as overhead azelaic and sebacic acids, respectively, with a final bottoms temperature of the order of 295° F. The bottoms stream from distillation column 117 contains principally the higher dicarboxylic acids having from about 11 to about 17 carbon atoms per molecule which are taken off as a cut rather than being separated into individual acids, however, it is of course obvious that additional distillation columns such as those exemplified could be provided to separate this higher dicarboxylic acid cut into individual components.

Returning to FIG. 1, the hydrocarbon phase from separator 62, treatment of which has not been discussed in detail previously, contains unreacted paraffin as well as higher carboxylic acids which are not water soluble, such acids including the higher dicarboxylic acids as well as higher monocarboxylic acids. Separation of the acids from the non-acid materials is accomplished typically in the apparatus shown in FIG. 3 by saponifier 125 where the stream is mixed with concentrated caustic solution (30-35 percent) and then diluted followed by decantation in separator 126. The soaps thus obtained are treated with mineral acid such as H₂SO₄ in acidifier 127, to spring the acids and the organic acids are separated from the sodium sulfate by-product in separator 128. The spectrum of acids resulting is resolved into individual acids and ranges of acids as desired for product as exemplified by distillation 129 which provides a high boiling cut of C₁₁-C₁₈ dicarboxylic acids and a lower boiling cut of C₁₁-C₁₈ monocarboxylic acids.

The foregoing arrangement for the recovery of dicarboxylic acids provides a substantial improvement of prior dicarboxylic acid recovery schemes which in general do not withdraw the dicarboxylic acids prior to saponification and hence place considerable load and expense upon the saponification and acidification components of the overall acid plant and which complicate the recovery of monocarboxylic acids which in many instances may constitute the principal desired product acids of such a plant, the

dicarboxylic acids being secondary products. Careful control of the conditions at each point of separation permit the removal of acids in groups to minimize the number of separations required and thereby improve the economics of the overall process.

EXAMPLE I

A normal paraffin hydrocarbon mixture having from 14 to 18 carbon atoms per molecule is oxidized by the passage of air therethrough for 6 hours at 150° C. using 1 percent tertiary butyl peroxide as a catalyst. The conversion is 55 percent (molecules oxygenated).

The oxidate is hydrogenated at 190° C. and 400 p.s.i.g. using nickel on activated clay catalyst for 4 hours.

The hydrogenated oxidate is distilled, the overhead stream extracted with water to separate hydrocarbon for recycle, extracted with hydrocarbons and lower acids recovered. The bottoms stream is extracted with water yielding a water phase and a hydrocarbon phase in the ratio of about 1:10 based on acid content of the streams.

The first separation (67) is conducted at 100° C.

The second separation (72-73) is conducted at 60° C.

Separation (79-80) is also at 60° C.

Separation (84-85) is at 15° C.

Separation (92-93) is at 15° C.

Extraction-separation (96-97) is at 100° C.

Separation (101-102) is at 90° C.

Extraction-separation (106-108) is at 100° C.

Melter (111) temperature is 120° C.

EXAMPLE II

The following illustrates the sizes of the stream involved in producing acids of the quantity of each type shown.

Fig. 1

Stream:	Pounds
Water Phase from 62	6,547

Fig. 2

Water Removed (Evap. 65)	3,355
Concentrate (To Sep. 67)	3,192
Liquor I	2,450
Crystals I	742
Water Removed (Evap. 70)	503
Concentrate (To Sep. 73)	1,947
Liquor II	1,363
Crystals II	584
Liquor V	262
Feed (To Evap. 76)	1,625
Water Removed (Evap. 76)	100
Concentrate (To Sep. 80)	1,525
Liquor III	1,342
Crystals III	183
Liquor IV	885
Crystals IV	457
Oxalic Acid	240
Succinic Acid	217
Water Removed (Evap. 89)	250
Liquor V	262
Crystals V	373
Malonic Acid	160
Glutaric Acid	213

Fig. 3

Liquor VII (Part to Ext. 96)	125
Mixture (To Sep. 97)	709
Liquor VI	279
Crystals VI	430
To Mixer 99	
Water	156
Liquor VIII	261
Liquor VI	279
Mixer 99 Effluent	696
Liquor VII (Total)	500
Liquor VII (To Ext. 106)	125

FIG. 3—Continued

	Pounds
Liquor VII (To Mixer 61 of FIG. 1) -----	250
Liquor VII (To Ext. 96) -----	125
Adipic Acid -----	196 5
Crystals VI (To Ext. 106) -----	430
Crystals III (To Ext. 106) -----	183
Effluent (Ext. 106) -----	738
Liquor VIII -----	261
Crystals VIII -----	477 10
Crystals I -----	742
Effluent (Melter 111) -----	1,219
C ₇ -C ₁₀ Monobasic Cut -----	52
Pimelic Acid -----	254
Suberic Acid -----	288 15
Azelaic Acid -----	295
Sebacic Acid -----	165
C ₁₁ -C ₁₇ Dibasic Acids (from Dist. 117) -----	165
From the foregoing it is obvious that the invention may be practiced in numerous ways and that the invention is not to be limited except as defined in the appended claims. What is claimed is:	20
1. A process for producing dicarboxylic acids comprising,	25
oxidizing a normal paraffin hydrocarbon having from 12 to 20 carbon atoms per molecule,	
hydrogenating the oxidate to remove hydroxyl and carbonyl groups,	
removing by distillation the monocarboxylic acids having up to about 6 carbon atoms per molecule,	30
extracting with water the water soluble acids remaining, partially crystallizing the mixture of water soluble acids at a temperature from about 85° C. to about 110° C. to provide a mixture of crude pimelic, suberic, azelaic, and sebacic acids, together with monocarboxylic acids and dicarboxylic acids having from about 7 to about 18 carbon atoms per molecule,	35
removing the crystallized acids,	
partially crystallizing the liquid residue from the preceding step at a temperature from about 45° C. to about 85° C. to provide crude adipic acid,	40
removing the crude adipic acid,	
partially crystallizing the liquid residue from the preceding step at a temperature from about 0° C. to about 45° C. and at a concentration of malonic and glutaric which is less than saturated to provide mixed oxalic and succinic acids,	45
removing the oxalic and succinic acids,	
crystallizing the liquid residue from the preceding step to provide mixed malonic and glutaric acids, and removing the malonic and glutaric acids.	50
2. A process for producing dicarboxylic acids comprising,	
oxidizing a normal paraffin hydrocarbon having from 12 to 20 carbon atoms per molecule,	55
hydrogenating the oxidate to remove hydroxyl and carbonyl groups,	
removing by distillation the monocarboxylic acids having up to about 6 carbon atoms per molecule,	60
extracting with water the water soluble acids remaining, partially crystallizing the mixture of water soluble acids at about 100° C. to provide a mixture of crude pimelic, suberic, azelaic, and sebacic acids, together with monocarboxylic acids having from about 7 to about 10 carbon atoms per molecule and dicarboxylic acids having from about 7 to about 18 carbon atoms per molecule,	65
removing the crystallized acids,	
partially crystallizing the liquid residue from the preceding step at about 60° C. to provide crude adipic acid,	70
removing the crude adipic acid,	
partially crystallizing the liquid residue from the preceding step at about 15° C. and at a concentration	75

of malonic and glutaric which is less than saturated to provide mixed oxalic and succinic acids, removing the oxalic and succinic acids, concentrating the solution, crystallizing the liquid residue from the preceding step to provide mixed malonic and glutaric acids, and removing the malonic and glutaric acids.

3. A process for producing dicarboxylic acids comprising,

oxidizing a normal paraffin hydrocarbon having from 12 to 20 carbon atoms per molecule, hydrogenating the oxidate to remove hydroxyl and carbonyl groups, removing by distillation the monocarboxylic acids having up to about 6 carbon atoms per molecule, extracting with water the water soluble acids remaining, partially crystallizing the mixture of water soluble acids at a temperature from about 85° C. to about 110° C. to provide a mixture of crude pimelic, suberic, azelaic and sebacic acids, together with monocarboxylic acids having from about 7 to about 10 carbon atoms per molecule and dicarboxylic acids having from about 7 to about 18 carbon atoms per molecule,

removing the crystallized acids, partially crystallizing the liquid residue from the preceding step at a temperature from about 45° C. to about 85° C. to provide crude adipic acid, removing the crude adipic acid, secondarily crystallizing the liquid from the foregoing partial crystallization of adipic acid in a second stage at about the same temperature to remove additional adipic and higher acids therefrom, partially crystallizing the liquid residue from the preceding step at a temperature from about 0° C. to about 45° C. and at a concentration of malonic and glutaric which is less than saturated to provide mixed oxalic and succinic acids, removing the oxalic and succinic acids, crystallizing the liquid residue from the preceding step to provide mixed malonic and glutaric acids, and removing the malonic and glutaric acids.

4. A process for producing dicarboxylic acids comprising,

oxidizing a normal paraffin hydrocarbon having from 12 to 20 carbon atoms per molecule, hydrogenating the oxidate to remove hydroxyl and carbonyl groups, removing by distillation the monocarboxylic acids having up to about 6 carbon atoms per molecule, extracting with water the water soluble acids remaining, partially crystallizing the mixture of water soluble acids at about 100° C. to provide a mixture of crude pimelic, suberic, azelaic, and sebacic acids, together with monocarboxylic acids having from about 7 to about 10 carbon atoms per molecule and dicarboxylic acids having from about 7 to about 18 carbon atoms per molecule,

removing the crystallized acids, partially crystallizing the liquid residue from the preceding step at about 60° C. to provide crude adipic acid, removing the crude adipic acid, secondarily crystallizing the liquor from the foregoing partial crystallization of adipic acid in a second stage at about the same temperature to remove additional adipic and higher acids therefrom, partially crystallizing the liquid residue from the preceding step at about 15° C. and at a concentration of malonic and glutaric which is less than saturated to provide mixed oxalic and succinic acids, removing the oxalic and succinic acids, crystallizing the liquid residue from the preceding step to provide mixed malonic and glutaric acids, and removing the malonic and glutaric acids.

5. A process for producing dicarboxylic acids comprising,
 oxidizing a normal paraffin hydrocarbon having from 12 to 20 carbon atoms per molecule,
 hydrogenating the oxidate to remove hydroxyl and carbonyl groups,
 removing by distillation the monocarboxylic acids having up to about 6 carbon atoms per molecule,
 extracting with water the water soluble acids remaining,
 partially crystallizing the mixture of water soluble acids at a temperature from about 85° C. to about 110° C. to provide a mixture of crude pimelic, suberic, azelaic, and sebacic acids, together with monocarboxylic acids having from about 7 to about 10 carbon atoms per molecule and dicarboxylic acids having from about 7 to about 18 carbon atoms per molecule,
 removing the crystallized acids,
 partially crystallizing the liquid residue from the preceding step at a temperature from about 45° C. to about 85° C. to provide crude adipic acid,
 removing the crude adipic acid,
 secondarily crystallizing the liquor from the foregoing partial crystallization of adipic acid in a second stage at about the same temperature to remove additional adipic and higher acids therefrom,
 melting and recrystallizing crude adipic acid removed in the preceding crystallizations to extract purer adipic acid therefrom,
 partially crystallizing the liquid residue from the crude adipic acid separation steps at a temperature from about 0° C. to about 45° C. and at a concentration of malonic and glutaric which is less than saturated to provide mixed oxalic and succinic acids,
 removing the oxalic and succinic acids,
 crystallizing the liquid residue from the preceding step to provide mixed malonic and glutaric acids,
 and removing the malonic and glutaric acids.

6. A process for producing dicarboxylic acids comprising,
 oxidizing a normal paraffin hydrocarbon having from 12 to 20 carbon atoms per molecule,
 hydrogenating the oxidate to remove hydroxyl and carbonyl groups,
 removing by distillation the monocarboxylic acids having up to about 6 carbon atoms per molecule,
 extracting with water the water soluble acids remaining,
 partially crystallizing the mixture of water soluble acids at about 100° C. to provide a mixture of crude pimelic, suberic, azelaic, and sebacic acids, together with monocarboxylic acids having from about 7 to about 10 carbon atoms per molecule and dicarboxylic acids having from about 7 to about 18 carbon atoms per molecule,
 removing the crystallized acids,
 partially crystallizing the liquid residue from the preceding step at about 60° C. to provide crude adipic acid,
 removing the crude adipic acid,
 secondarily crystallizing the liquor from the foregoing partial crystallization of adipic acid in a second stage at the same temperature to remove additional adipic and higher acids therefrom,
 melting and recrystallizing crude adipic acid removed in the preceding crystallizations to extract purer adipic acid therefrom,
 partially crystallizing the liquid residue from the crude adipic acid separation steps at about 15° C. and at a concentration of malonic and glutaric which is less than saturated to provide mixed oxalic and succinic acids,
 removing the oxalic and succinic acids,

crystallizing the liquid residue from the preceding step to provide mixed malonic and glutaric acids,
 and removing the malonic and glutaric acids.

7. A process for producing dicarboxylic acids comprising,
 oxidizing a normal paraffin hydrocarbon having from 12 to 20 carbon atoms per molecule,
 hydrogenating the oxidate to remove hydroxyl and carbonyl groups,
 removing by distillation the monocarboxylic acids having up to about 6 carbon atoms per molecule,
 extracting with water the water soluble acids remaining,
 partially crystallizing the mixture of water soluble acids at a temperature from about 85° C. to about 110° C. to provide a mixture of crude pimelic, suberic, azelaic, and sebacic acids, together with monocarboxylic acids having from about 7 to about 10 carbon atoms per molecule and dicarboxylic acids having from about 7 to about 18 carbon atoms per molecule,
 removing the crystallized acids,
 partially crystallizing the liquid residue from the preceding step at a temperature from about 45° C. to about 85° C. to provide crude adipic acid,
 removing the crude adipic acid,
 secondarily crystallizing the liquid from the foregoing partial crystallization of adipic acid in a second stage at about the same temperature to remove additional adipic and higher acids therefrom,
 partially crystallizing the liquid residue from the preceding step at a temperature from about 0° C. to about 45° C. and at a concentration of malonic and glutaric which is less than saturated to provide mixed oxalic and succinic acid,
 removing the oxalic and succinic acids,
 crystallizing the liquid residue from the preceding step to provide mixed malonic and glutaric acids,
 removing the malonic and glutaric acids,
 and recycling the mother liquor from the separation of malonic and glutaric acids as additional feed to the preceding secondarily crystallizing step whereby additional acids are recovered.

8. A process for producing dicarboxylic acids comprising,
 oxidizing a normal paraffin hydrocarbon having from 12 to 20 carbon atoms per molecule,
 hydrogenating the oxidate to remove hydroxyl and carbonyl groups,
 removing by distillation the monocarboxylic acids having up to about 6 carbon atoms per molecule,
 extracting with water the water soluble acids remaining,
 partially crystallizing the mixture of water soluble acids at about 100° C. to provide a mixture of crude pimelic, suberic, azelaic, and sebacic acids, together with monocarboxylic acids having from about 7 to about 10 carbon atoms per molecule and dicarboxylic acids having from about 7 to about 18 carbon atoms per molecule,
 removing the crystallized acids,
 partially crystallizing the liquid residue from the preceding step at about 60° C. to provide crude adipic acid,
 removing the crude adipic acid,
 secondarily crystallizing the liquid from the foregoing partial crystallization of adipic acid in a second stage at about the same temperature to remove additional adipic and higher acids therefrom,
 partially crystallizing the liquid residue from the preceding step at about 15° C. and at a concentration of malonic and glutaric which is less than saturated to provide mixed oxalic and succinic acid,
 removing the oxalic and succinic acids,

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crystallizing the liquid residue from the preceding step to provide mixed malonic and glutaric acids, removing the malonic and glutaric acids, and recycling the mother liquor from the separation of malonic and glutaric acids as additional feed to the preceding secondarily crystallizing step whereby additional acids are recovered. 5

9. A process for recovering carboxylic acids from mixtures thereof with hydrocarbons comprising, 10
 distilling the mixture to produce a light fraction containing lower monocarboxylic acids having up to about 6 carbon atoms per molecule and a heavy fraction containing other acids and hydrocarbons, extracting the light fraction with water to separate the acids and hydrocarbons contained therein, 15
 extracting the acid phase from the preceding step with hydrocarbon to separate the acid from the residual water,

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extracting the heavy fraction with water to provide separate hydrocarbon and water phases, subjecting the water phase from the heavy fraction to successive crystallization and recrystallization at a plurality of different temperatures whereby the acids contained therein are separated into individual components and cuts, saponifying the hydrocarbon phase to separate acids and non-acids, and recovering the acids and acid cuts separated.

References Cited

UNITED STATES PATENTS

2,800,506	7/1957	Millidge et al. -----	260—533
2,824,134	2/1958	Hill et al. -----	260—533

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