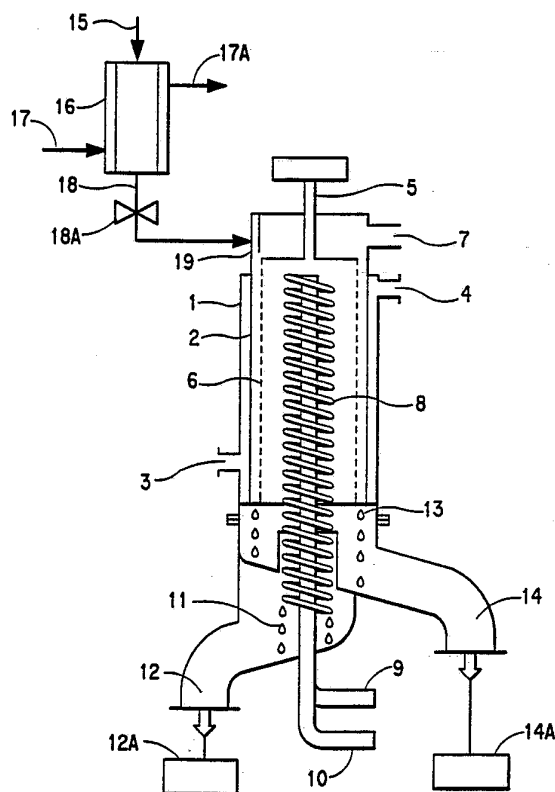




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(54) Title: THIN FILM DEPOLYMERIZATION TO DIMERIC CYCLIC ESTERS



(57) Abstract

A process and an apparatus for depolymerizing a thin film to form a dimeric cyclic ester. The process and apparatus afford rapid and substantially complete conversion to a dimeric cyclic ester, little or no decomposition by-products, and high yields of a quality product.

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- 1 -

TITLETHIN FILM DEPOLYMERIZATION
TO DIMERIC CYCLIC ESTERS

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FIELD OF THE INVENTION

This invention relates to a reduced pressure reactive distillation process for the preparation of dimeric cyclic esters. The process of the invention comprises depolymerizing thin films of an oligomer of a hydroxycarboxylic acid to form a dimeric cyclic ester and recovering the cyclic ester. The thin film process of the invention affords rapid and substantially complete conversion to a dimeric cyclic ester, low hold-up times, little or no decomposition to undesirable by-products, and high quality product in high yields.

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BACKGROUND OF THE INVENTION

Dimeric cyclic esters of hydroxycarboxylic acids such as glycolide (1,4-dioxane-2,5-dione) and lactide (1,4-dioxane-3,5-dimethyl-2,5-dione), are intermediates to high molecular weight polyhydroxycarboxylic acids which may be useful in biomedical and other applications because of their ability to be degraded biologically and hydrolytically to form physiologically and environmentally acceptable by-products.

A process for producing dimeric cyclic esters may be found in Aigner et al., European Patent Application Publication No. 264926. Aigner et al., discloses conducting a thermolysis depolymerization reaction continuously in a forced feed flow tube reactor (double screw extruder) under reduced pressure, while maintaining an increasing temperature gradient along its length. The dimeric cyclic ester product distills from the reaction mass through vapor ports located at the downstream end of the reactor, while the higher-boiling residue is extruded under the force-feed extrusion conditions.

It is an object of this invention to provide an improved process for converting low molecular weight oligomers or polymers of alpha-hydroxycarboxylic compositions to cyclic esters in short residence times and at high production rates.

It is another object of this invention to provide a process wherein the polymer of an alpha-hydroxycarboxylic composition is substantially completely converted to the cyclic ester, with substantially reduced racemization and other undesirable decomposition reactions.

SUBSTITUTE SHEET

- 2 -

It is a further object of this invention to provide a process which achieves rapid conversion to the dimeric cyclic ester while minimizing hold-up time in the reactor and exposure of the reaction mass and product to thermal stress.

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SUMMARY OF THE INVENTION

This invention is based on the discovery that conversion of an oligomer of an alpha-hydroxycarboxylic acid moiety (e.g., an oligomer of lactic acid), to a cyclic ester (e.g., lactide), proceeds more rapidly than heretofore believed when the reaction mass comprising the oligomer is spread as a thin liquid or molten film onto a surface which has been heated to depolymerization temperatures. Disposing the oligomer on the heated surface as a thin film, preferably one having a relatively large surface area to film thickness ratio, enables (1) heat to be transferred rapidly from the heating surface to the oligomer composition and, (2) reaction products (e.g., lactide) to be transferred rapidly through the oligomer film and vaporized rapidly from the oligomer surface (i.e., the reaction products are more volatile than the oligomer). This makes feasible a short residence time, continuous process providing high conversions and yields of the cyclic ester while reducing racemization and decomposition or other undesirable side reactions occurring.

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The invention is directed to an improved process for depolymerizing (thermolyzing) a depolymerizable oligomer of an alpha-hydroxycarboxylic acid composition to a dimeric cyclic ester under thin film distillation conditions by heating to effective depolymerization and distillation temperatures, whereby conversion of the oligomer to a vaporized cyclic ester is effected at short residence times.

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The invention relates to a process for converting an oligomer of an alpha-hydroxycarboxylic acid, an alkyl ester or salt thereof, comprising (1) disposing a thin liquid film of a preformed oligomer on a heated surface in a reaction zone, (2) maintaining the surface at a temperature sufficient to heat the film to a depolymerization temperature and convert the oligomer to dimeric cyclic ester while maintaining the reaction zone at a reduced pressure sufficiently low to form a vapor product stream containing the dimeric cyclic ester, and (3) recovering the product stream.

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The process of the invention is particularly applicable to preparing lactide, including L-lactide, in high yield and at a high conversion rate from an oligomer of lactic acid or an ester or a nitrogen base salt thereof.

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- 3 -

In one embodiment of the invention, the vapor product stream is cooled, condensed and collected as a liquid. In a key aspect of this embodiment, the oligomer film is formed and depolymerized continuously, and the vaporized product is collected continuously. In another aspect of the continuous process embodiment, the feed rate of the oligomer to the heated surface, the thickness of the oligomer film, the temperature and the pressure are coordinated and controlled such that the depolymerization proceeds substantially completely to form a vaporized product. Minor quantities, if any, of a residue (e.g., so-called heel) may also be formed, but the presence of a residue does not affect overall performance of the process. The residue can be removed periodically and recycled or hydrolyzed as hereinafter described. For best results, thin film depolymerization is conducted, according to the invention, within a wiped-film evaporator.

The invention is a reactive distillation process comprising a series of steps which include thermolysis/depolymerization of an open-chain poly (hydroxycarboxylic) acid composition to a more volatile cyclic reaction product, followed by vaporization of the cyclic product from the thermolyzing mass and condensation to recover the cyclic ester product.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a sectional view of a wiped film evaporator with an internal condenser.

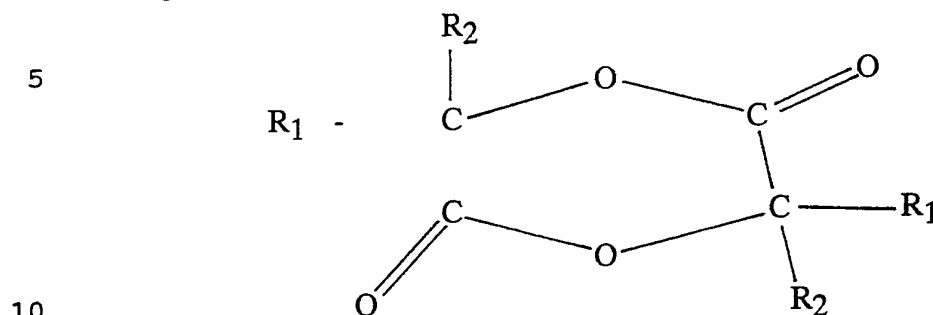
Fig. 2 is a sectional view of the wiped film evaporator of Fig. 1 which is coupled with an external condenser.

Fig. 3 is a schematic block diagram of the invention.

- 4 -

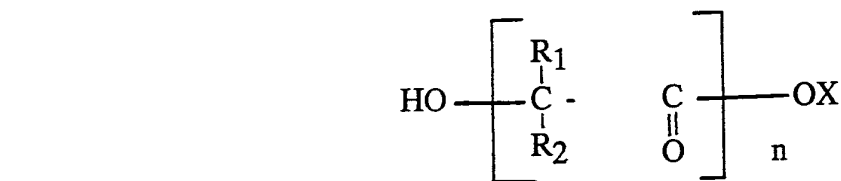
DETAILED DESCRIPTION OF THE INVENTION

The invention is directed to a process for preparing a cyclic ester having the formula:



wherein R1 and R2 are independently hydrogen or an aliphatic hydrocarbyl radical having 1 to 6 carbon atoms. According to a key aspect of the process, an oligomer of an alpha-hydroxycarboxylic acid, an ester or a nitrogen base salt thereof, is introduced as a thin molten film into a reaction surface in a reaction zone which is maintained at a reduced pressure and an elevated temperature. The pressure and temperature within the reaction zone are maintained such that the oligomer is depolymerized and a thermolysis product, or products, are vaporized to form a product stream containing the cyclic ester. The product stream may be recovered by any suitable method which does not adversely affect the cyclic ester. In some aspects of the invention, the product stream may be condensed which may be followed by one or more of redistillation, extraction and/or crystallization from a solvent to recover the desired cyclic ester product.

The oligomeric feed material may comprise an oligomer of an oligomerizable alpha-hydroxycarboxylic acid, ester and/or a nitrogen base salt thereof, which has the formula:



wherein n is an integer of 2 to 50; X is independently H, R3 or a cationic group HA; R1, R2, and R3 are independently H or a C1-C6 hydrocarbyl radical; and "A" is a nitrogen base. Preferably, R1, R2 and R3, when other than H in the above formula, is an alkyl group. More preferably, R1 and R2 are H or methyl, as in glycolic acid (R1=R2=H) and lactic acid (R1=H, R2=methyl). The cationic group HA is preferably derived from a nitrogen base, such as ammonia or an alkyl amine, and preferably is ammonia or a tertiary amine, such as

- 5 -

trimethylamine, triethylamine, methyldiethylamine, tripropylamine, tributylamine, etc.

The degree of acceptable polymerization (i.e., the value of n) and the resultant molecular weight can vary widely so long as the oligomer may be rendered molten and depolymerized at the operating temperature. For best results, the value of n is in the range of from about 5 to about 30 (e.g., not more than about 25) and normally between about 10 and 15. The value of n tends to increase during the course of the depolymerization reaction so that any heel (i.e., polymeric residue) remaining upon completion of the reaction usually has a greater degree of polymerization than the starting oligomer. The heel may be recycled to the reactor in accordance with the invention so long as the oligomer may be rendered molten and is depolymerizable. Alternatively, the heel can be hydrolyzed to lower molecular weight alpha-hydroxy carboxylic acids, including the monomeric acid, which can be re-polymerized to oligomers of the desired degree of polymerization for reuse in the process.

The oligomer should generally be free of dissolved gases, solvents or other low boiling components to avoid or minimize the possibility of film deterioration resulting from bubbling and flashing of the film when subjected to a reduced operating pressure. Also, the oligomer is preferably preheated at or close to the operating temperature before it is fed to the reaction zone of the evaporator.

The depolymerization process is advantageously carried out in a continuous manner using a thin film evaporator. The thin film evaporator may comprise a heated cylindrical or tapered tubular reactor which includes means for distributing the oligomer over the heated inner surface of the reactor. In one aspect of the invention, the tubular reactor includes a series of rotatable wiper elements that maintain a close clearance from the wall or ride upon a film of liquid on the wall. In operation of such a reactor, the oligomer is continuously fed to and disposed onto the heated surface of the reactor wall as a thin liquid film. For best results, the thin film is disposed onto the heated surface in a manner sufficient to provide a relatively large surface area and a uniform thickness. For example, the film thickness should be as thin as can be practicably attained, and may range from about 0.05 to at least about 1.0mm, and normally about 0.2 through 0.5mm thick. For best results, the thickness of the thin film will range from about 0.3 to 1mm. Apparatuses which are acceptable for creating continuous depolymerization conditions are exemplified by:

SUBSTITUTE SHEET

- 6 -

A) A falling film evaporator, wherein the molten/liquified oligomer flows downward along heated walls of the evaporator. The quality of the film that forms depends primarily on the force of gravity, the viscosity of the oligomer and its flow rate along the heated surface. For best results, a falling film evaporator of the wiped film type is employed and equipped with means for spreading the incoming oligomer horizontally and vertically on the heat surface so as to create a thin film having a substantially uniform thickness and a relatively large surface area. The ratio of surface area to film thickness is not critical. However, in certain aspects of the invention it is desirable to create a high surface area to film thickness ratio since for a given thickness a greater ratio should increase the heat transfer from the heating means to a greater quantity of the liquid oligomer film, enhance the mass transfer of the depolymerization products through and out of the film thereby into the reduced pressure space above the film as vapor, and result in a greater quantity of product being formed in a given time period.

B) A desirable wiped-film evaporator for carrying out the process of the invention is equipped with rotating wiper elements that can be operated at various speeds of rotation and adjusted to provide different spacings between the heated evaporator wall and the wiper blades. The wiper blade spacing determines film thickness, while wiper rotation rate and oligomer feed rate determine the rate of film formation. Suitable wiper spacing (e.g., for appropriate film thickness) and speed of rotation are readily determined by trial for any particular oligomer composition, oligomer viscosity and other process conditions (e.g., temperature, pressure, etc.)

The vapor product stream produced on depolymerizing the oligomer to volatile products in the evaporator, is preferably contacted with a condensing surface, maintained at a temperature such that the product stream condenses as a liquid, which is allowed to drain into a receiver. The condensing surface may comprise an internal or an external condenser or a combination of the two which is discussed below in more detail in connection with Figs. 1 and 2. For example, the wiped film evaporator may include a heated surface which surrounds and is spaced apart from an internal condenser. The wiped-film evaporator may also be connected to an external condenser which functions as a substitute for or as a supplement to the internal condenser. The surface area of the condensing surface may be modified to control the manner in which the product stream is condensed. For example, the surface area of a coiled tube condenser may be increased by decreasing the diameter of the tube and

SUBSTITUTE SHEET

- 7 -

increasing the number of coils. The vapor product stream normally may comprise the dimeric cyclic ester and other volatiles, including open-chain hydroxycarboxylic acids (e.g., lactic acid, lactoyllactic acid, etc). The condensed vapor product is readily separated into its constituents using methods such as
5 distillation, extraction, crystallization, etc.

The process of this invention is generally conducted in the presence of a catalyst, which may be included in the oligomeric reactant before it is fed to the evaporator. The catalyst can be any catalyst which is suitable for promoting the thermolysis of the oligomers to cyclic esters. Suitable catalysts are
10 generally metals or compounds of metals of groups IV, V and VIII of the Periodic Table. Preferred are metals of groups IV, notably Sn as the metal (powdered), oxide, halogenide or carboxylate, or V, notably Sb, usually as the oxide Sb_2O_3 . Preferred herein are Sn (II) carboxylates, especially those that are soluble in the molten oligomer and exemplified by stannous bis(2-
15 ethylhexanoate), commonly referred to as stannous octoate.

The catalyst will be employed in catalytically-effective amounts, which can vary widely depending upon the particular feed material employed and the reaction conditions. The optimum catalytically-effective amounts for any particular system can readily be determined through trial runs. For example,
20 with stannous octoate as the catalyst, the quantity of catalyst will generally be such that the reaction mass contains from about 0.01 to about 5% by weight, usually from about 0.3 to 3% and for best results, at least about 1%. Higher catalyst loadings are more desirable because oligomer residence time decreases with increases in the initial catalyst concentration, thereby improving the dimeric
25 cyclic ester production rate.

In one aspect of the invention, it may be desirable to admix a solvent of the cyclic ester with the oligomer before the oligomer is introduced into the evaporator. A suitable solvent must be substantially inert under the depolymerization process conditions and be generally equal to and/or less
30 volatile than the cyclic ester. A solvent can improve the fluidity of the oligomer and maintain the cleanliness of the heating wall within the wiped-film evaporator. A suitable solvent having a volatility generally equivalent to the cyclic ester may also serve to maintain the cleanliness of the condenser by washing cyclic ester from the condenser surface.

35 Suitably effective temperatures in the evaporator can vary widely provided the temperature is below the decomposition temperature of the dimeric cyclic ester being formed. Normally, the temperature is in the range of from about

- 8 -

200°C to 290°C. The optimum temperature range for any particular oligomer-to-cyclic ester conversion will vary with the composition of the oligomer. For example, for the production of L-or D- lactide the temperature is usually in the range from about 250°C through about 270°C and, for glycolide from about
5 260°C through 280°C .

The surface of the evaporator's heating zone can be heated by any expedient means. The heating zone is advantageously constructed of a thermally conductive material so that heat can be supplied from an outside source through the wall of the heating zone to its internal evaporation surface and thus heat the
10 oligomer film to depolymerization temperatures. Heat may be supplied, for example, electrically by wrapping the outside of the heating zone with heating tape or by jacketing the zone with an electrically-heated mantle. Alternatively, the heating zone may be jacketed such that hot oil may be circulated through it and in this way bring the internal heating surface to the desired temperature. If
15 desired, thermocouples can be placed at the external surface of the evaporator's heating zone to monitor and record the depolymerization temperature.

The depolymerization process is carried out under subatmospheric pressures which are consistent with the vapor pressure of the cyclic ester being recovered at the operating (depolymerizing) temperature. The pressure can vary
20 from below about 1mm of Hg upwards and is normally below about 20mm of Hg. Generally, the pressure is the range of about 1 to 5mm of Hg.

An important aspect of the invention is that one or more of the following process conditions, such as the oligomer composition, oligomer viscosity, oligomer feed rate, speed of film formation (e.g., rotation rate of the
25 wiper blades), film thickness, temperature, pressure and oligomer catalyst loading, can be coordinated such that substantially all the oligomer being fed is converted to a vapor product stream rapidly and substantially completely with little or no heel formation. Control of these process conditions makes feasible a short residence time continuous process affording high conversion of oligomer
30 and high yields of the desired dimeric cyclic ester with little or no occurrence of racemization, decomposition or other undesirable side reactions, such as charring. Residence times can be extremely short, i.e., generally are a matter of minutes, often between about 1 and 10 minutes. While it may be desirable to achieve as high a conversion/ production rate as possible by eliminating heel
35 formation, it is generally advisable to maintain the depolymerization conditions such that a small quantity of oligomer heel can be removed from the evaporator as the reaction proceeds since the heel retains the catalyst, which might

otherwise leave deposits on the evaporator walls. The heel may be recycled directly to the evaporator or it may first be hydrolyzed to lower molecular weight alpha-hydroxy carboxylic acids which may be recycled along with the catalyst to form additional oligomer which is then used for producing the cyclic ester.

5 The characteristics of the heel which is formed, determines the degree to which it may be recycled. The practicality of recycling the heel typically is related to the degree to which it is polymerized. For example, heels which have a relatively high degree of polymerization (as shown by a high
10 molecular weight) are more difficult to recycle due in part to the reduced quantity of hydroxyl groups on the end of the polymer chain. Any heel which may be produced in the process will have had a short residence time in the wiped-film evaporator and, therefore, possess relatively low molecular weights which typically permits these heels to be directly recycled or readily transformed
15 into a recyclable form.

15 The flow of oligomer to the heated wall of the wiped-film evaporator can vary widely depending on the oligomer, its viscosity and its temperature (viscosity decreasing with increasing temperature); also on the depolymerization temperature and configuration of the evaporator itself. The flow of oligomer into the wiped film evaporator should be sufficient for the
20 oligomer to form a film under gravitational flow onto the surface of the heated wall, but it should not be so fast as to flood the evaporator. The oligomer flow rate should be coordinated with the depolymerization temperature so that a thin film is established and maintained throughout the run and depolymerization proceeds such that most, if not substantially all the oligomer, is depolymerized to
25 the desired cyclic ester product. Further, the flow rate of the oligomer should also be coordinated with the rotation rate of the wiper blades (i.e., the wiper blades cause the oligomer to form a film along the heated surface of the wiped-film evaporator). For example, a relatively high oligomer flow rate should be accompanied with a rapid wiper blade rotation rate to ensure effective
30 depolymerization of the oligomer without excessive charring or heel formation. However, in some cases, it is advantageous to leave a minor proportion of oligomer unconverted so that flowable "heel" can be removed and in this way maintain a clean heating wall (i.e., a heating wall substantially free of decomposition products and deposits).

35 The invention may be better understood with reference to the drawings.

- 10 -

The apparatus of Fig. 1 consists essentially of a jacketed cylindrical evaporator 1 evacuable to reduced pressures through line 7 by a vacuum pump not shown. Evaporator 1 contains internal condenser 8 spaced apart from inside wall 2 of evaporator 1 and a rotatable cylindrically shaped wiper blade mechanism 5 disposed between wall 2 and condenser 8. Wiper blade mechanism 5 has a plurality of wiper blades 6 adapted to spread liquid oligomer evenly and uniformly over wall 2; the wiper blade mechanism 5 also has a plurality of openings 6A between the blades and along the circumference of the cylindrical shape formed by the blades, whereby wall 2 communicates with condenser 8 through the combined 6A openings. The spacing between wall 2 and blades 6 can be fixed or adjusted to provide a variety of wall-to-wiper blade spacings. Wiper blade mechanism 5 is rotatable at various controlled speeds by a motor drive not shown at 5A.

Evaporator wall 2 is heated from an external surface to operating temperatures by circulating appropriately hot oil through the jacket, the oil entering at 3 and exiting at 4.

Thermocouples placed at the jacket of 1 provides a measure of the temperature at wall 2. The depolymerization temperature developed at wall 2 is a function of the temperature of the heating fluid, which temperature is readily determined by trial for any particular oligomer.

The temperature of condenser 8 is controllable by circulating coolant through it via entering and leaving lines 9 and 10.

Evaporator 1 is adapted to receive molten oligomer from jacketed feed vessel 16. The oligomer, fed to 16 through line 15, is maintained molten by circulating sufficiently hot oil through the jacket, the oil entering at 17 and exiting at 17A. The temperature of the molten oligomer should be below but reasonably close to the depolymerization temperature. Valve 18A controls the feed rate of the molten oligomer to evaporator 1. Normally, valve 18A is adjusted such that about 500cc of oligomer will pass into the jacketed cylindrical evaporator in from about 45 minutes through about 2 hours. Deflector plate 19 is positioned to direct molten oligomer fed via line 18 to wall 2 of the evaporator so that it can flow under gravity down the wall and can be spread by wiper blades 6 vertically and horizontally to a substantially uniform thickness over the entire inside wall of the evaporator.

Depolymerization products vaporized from the oligomer heated to depolymerization temperatures at wall 2 pass through openings 6A, condense at least in part on condenser 8 and are collected as condensate 11, via line 12, in

SUBSTITUTE SHEET

- 11 -

receiver 12A. Molten material not converted to vapor collects as heel 13, via line 14, in receiver 14A.

Condensate 11 can be further processed by any means known to the art for recovering and further refining the cyclic ester product, if desired.

5 Similarly, the recovered "heel" may be recycled to the reactor for conversion to additional quantities of cyclic ester. If its degree of polymerization is higher than desired, it may be further processed to convert it to an oligomer having a more optimum degree of polymerization.

Fig. 2 incorporates the features of Fig. 1 and includes as well
10 external condenser 20 communicating with evaporator 1 through insulated line 7 (insulation not shown). Condenser 20 is cooled by a coolant (e.g., ethylene glycol, water, mixtures thereof, etc.) circulating through it via lines 21 and 22, and is so sized and placed as to condense substantially all vaporized product not condensed by condenser 8, condensate 23 passing through line 24 to receiver
15 24A. Uncondensed product vapor, if any, leaving condenser 20 through line 7A passes through cold trap 26 maintained at a low temperature, for example that provided by a solid CO₂ - alcohol mixture 27. Sensor 28 measures the reduced pressure established by the vacuum pump.

It should be noted that in the above representative thin film
20 evaporators the distance between the wall at which the oligomer is depolymerized and the condensing surface can vary widely. For example, in an evaporator of the internal condenser type it may be very small, for example, on the order of the mean free path of the dimeric cyclic ester depending on the operating pressure or it may be, as in evaporators with external condensers, quite
25 large, for example, many times the mean free path of the cyclic ester. For the present invention, it has been found that the distance between heating surface and condensing surface is not critical provided the pressure is sufficiently low and the depolymerization temperature is sufficiently high to ensure an adequate cyclic ester production rate. Optimum temperatures and pressures for a given
30 oligomer in a given evaporator are readily determined by trial. Evaporators with external condensers, which imply relatively large heating surface to condensing surface distances, are preferred herein for the more complete recoveries of the vapor products they provide.

Now referring to Fig. 3 which is a schematic block diagram of the
35 operation for producing the cyclic ester, concentrated aqueous lactic acid, preferably containing about 80-90% by weight lactic acid (e.g., 88% acid as is available commercially), is fed through line 31 to converter 32 where it is further

- 12 -

concentrated by distillation and polymerized to polylactic acid (PLA) with further removal of water-of-reaction by heating gradually to about 160°C, then to 175°C usually under reduced pressure or with a N₂ sweep. The aqueous distillate removed during this concentration and polymerization stage is passed through 33 to concentrator 34, where it is dehydrated to concentrated lactic acid for recycle. Polylactic acid produced in 32 is sent through 36 to a thin film evaporator 37, such as illustrated in Figs. 2 and 3, where it is converted to the corresponding dimeric cyclic ester (e.g., lactide), as described above. The condensed product produced in evaporator 37 containing lactide, minor proportions of lactic acid and still minor proportions of volatilized water-soluble oligomers generally having 2 to 3 lactic acid units, can be further processed/purified by solvent treatments. For example, the condensed product exits the thin film evaporator through 38 and enters an extractor 39, where it is extracted with a suitable solvent, for example acetone, to form a solution of lactide and its lactic acid value impurities.

With a water-miscible solvent such as acetone, the solution is concentrated to start precipitation of lactide, and diluted with water, preferably water cooled to 0-5°C, in an amount sufficient to precipitate the lactide substantially completely, leaving the lactic acid values in the aqueous solution. Lactide, substantially free of its impurities, is separated, as by filtration or centrifugation, removed through line 41 and purified further if desired, by washing, drying and recrystallization from non-reactive solvents (e.g., toluene). When a water-immiscible solvent is employed (e.g., methyl isobutyl ketone), the organic solution produced in 39, is thoroughly extracted with water in an amount sufficient to remove substantially all the lactic acid values from the solution, and the resulting aqueous phase separated from the organic. The lactide-containing organic phase is removed via line 40 and lactide recovered from the solution by any means known to the art (e.g., solvent evaporation), crystallization and recrystallization, as necessary or desired.

The aqueous solution containing substantially all the lactic acid values and residual organic solvent is sent through line 41 to concentrator 42 where any organic solvent present is stripped therefrom, and the aqueous solution concentrated for recycle (e.g., to 88% lactic acid), the organic solvent and excess water being removed via line 43, the recycle stream through 47. The polylactic acid residue remaining in the thin-film evaporator 37 is removed through 44. If necessary or desired, the residue (or heel) can be hydrolyzed back to monomeric (e.g., lactic acid), by passing it to hydrolyzer 45 where it is heated

SUBSTITUTE SHEET

- 13 -

with water at the boil until the residue is converted substantially completely to an aqueous solution.

The hydrolysate is filtered and concentrated, if necessary, to, for example, 88% lactic acid for recycle. Preferably, the proportion of water employed for hydrolysis will be sufficient to provide an hydrolysate having the desired lactic acid concentration. Also, one could use dilute aqueous lactic acid for hydrolysis. Lactic acid hydrolysate for recycle leaves hydrolyzer 45 through 47, is combined with the lactic acid recycle stream 48 (from 43) and 35 (from 34) to form combined stream 49, which is recycled to line 31, then to converter 2 along with make up concentrated lactic acid.

The overall operation, representing a single illustrative recycle stage, can be repeated to achieve a lined-out recycle process wherein the amount of recycle material will equal the amount of lactic acid material generated in each pass. Recycle of recovered lactic acid enables the quantity of fresh lactic acid feed to the converter to be reduced and the overall yield of lactide thereby increased.

The following examples are provided to illustrate, not limit the scope of the appended claims. Unless specified otherwise, commercially available materials were used to practice the following examples.

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EXAMPLES

A UIC Industries (Joliet, Illinois, USA) Model KDL-4 wiped film evaporator was used in each of the following examples. The evaporator included a vertically arranged cylindrical housing which possessed about 0.043 square meters of evaporator surface. The evaporator was modified to include an external condenser downstream from its internal condenser which is illustrated in Figure 2. The evaporator was jacketed for heating its evaporator surface with circulating hot oil and was also equipped with (a) a jacketed feed funnel, also heatable with circulating hot oil, (b) a feed means for metering molten oligomer into the evaporator at controlled rates, the feed being provided at the top and allowed to flow down the interior cylindrical wall of the evaporator, (c) glass-reinforced Teflon® polytetra-fluoroethylene rollers serving as rotating wiper blades for mechanically spreading the oligomer as a thin film both horizontally and vertically over the heated wall. The wiper blades were rotated by a Janke-Kunkel model no. RW20 drive mechanism which had a setting of 2.5. The wiper blade spacing was set to provide a film thickness of about 0.5mm. The unit

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- 14 -

included means for evacuating and maintaining the evaporator under reduced pressure.

EXAMPLE 1

5 A. An oligomer of lactic acid was prepared by gradually heating a mixture of about 1650 grams 88% L-lactic acid containing less than about 1% D-lactic acid and about 18.5 grams stannous octoate up to a temperature of about 180°C while a stream of N₂ gas was passed through the mass to facilitate removal of water. The process was continued until the oligomeric produced
10 show an average chain length of 10, determined by titration in methanol with methanolic sodium methoxide using phenolphthalein as the indicator. The resultant oligomer contained about 0.69% by weight of the stannous octoate catalyst.

15 B. The oligomer prepared in step (A) above, was depolymerized under the following conditions:

The wiper roller of the wiped film evaporator was set at agitation setting of about 2.5; about 260°C oil was circulated through the evaporator jacket and about 150°C oil through the feed funnel jacket. Hot water was circulated through the condensers to a temperature of about 90°C and the
20 evaporator was evacuated and maintained at about 1 mm of Hg pressure. Preheated (150°C) molten oligomer was fed to the evaporator at a rate of about 273 grams/hour. Distillate from the evaporator surface was collected as drainage from the condensers at the rate of about 234.5 grams/hour. A heel was drained from the heated evaporator wall, was collected at the rate of about 35.5
25 grams/hour. The wiped-film evaporator was operated for about 85 minutes. The residence time in the reactor was about 6.0 minutes.

The ratio of the distillate collection rate to the oligomer feed rate was about 85.9% $[(234.5/273) \times 100]$. The ratio of the sum of the distillate and heel collection rates to the feed rate was 98.9% $[(270/273) \times 100]$ which
30 indicated substantially complete recovery of the thermolysis products (distillate).

The distillate contained about 69.5% L-lactide, 6.5% meso-lactide and 0.04% D-lactide, which was determined by high pressure liquid chromatography. The remainder of the distillate consisted essentially of lactic acid and volatilized water-soluble lactic acid oligomers amounting to about 1130
35 milliequivalents of acidity per kilogram of distillate. The above lactide content on a 100% basis, corresponds to about 91.2% L-lactide, 8.3% meso-lactide and 0.5% D-lactide.

SUBSTITUTE SHEET

- 15 -

Although the data above indicate that some racemization had occurred during the depolymerization step, the proportion of meso-isomer was acceptable.

5 EXAMPLE 2

The procedure of Example 1 was repeated except that (a) the lactic acid was oligomerized to an average chain length of 18 and the oligomer contained about 0.59% by weight of the stannous octoate, (b) the oligomer feed rate was about 255 g/hr, (c) the distillate recovery rate was about 244 g/hr and
10 (d) the heel recovery rate was nil. Thus, the ratio of distillate rate to feed rate was about 95.7%.

The distillate contained about 77.6% L-lactide, 6.1% meso-lactide and 0.2% D-lactide. The remaining 16.1% of distillate consisted of lactic acid and volatilized lactic acid oligomers corresponding to about 650 milliequivalents
15 of acidity/kg of distillate. On a 100% basis, the lactide content correspond to about 92.5% L-, 7.3% meso and 0.24% D-lactide.

EXAMPLE 3

Example 1 was repeated except that (a) the oligomer contained
20 2.9% by weight of stannous octoate, (b) 170°C oil was circulated through the feed funnel jacket and 270°C oil through the evaporator jacket, (c) the feed rate of oligomer to the evaporator was 941 grams/hour.

Distillate was collected at the rate of 731 grams/hour, and unconverted material (heel) at 197 grams/hour. The duration of the run was 0.6
25 hours. The residence time in the reactor was about 4 minutes.

The ratio of the distillate collection rate to the oligomer feed rate was 77.7% [731/941 X 100]; the ratio of the sum of the distillate and heel collection rates to the feed rate was 98.6% [928/941 X 100].

The distillate was found to contain 64.4% L-lactide, 5.92%
30 mesolactide and 0.62% D-lactide, by HPLC, and 1334 me/kg of acidity. The lactide content on a 100% basis corresponded to 90.8% L-, 8.3% meso- and 0.8% D-lactide.

EXAMPLE 4

35 This example was carried out in a 4" wiped film still made by Pope Scientific Co., Menomonee Falls, WI. The still contained a jacketed vertical

SUBSTITUTE SHEET

- 16 -

evaporator section equipped with a variable speed drive film wiper mechanism and coupled to an external condenser.

5 A lactic acid oligomer was prepared by gradually heating 2000 grams of 88% L-lactic acid and 20 grams of stannous octoate to 180°C and holding at that temperature for 1 hour. The pressure was reduced and heating at 180°C was continued to remove water until the resulting oligomer showed an average chain length of 11.8.

10 The evaporator was evacuated and heated by circulating 245°C oil through its jacket. 1344 grams of the oligomer was fed to the evaporator at the rate of about 1209 grams/hour over a period of about 50 minutes. During this time, the pressure in the evaporator ranged between 2.5 and 10mm of Hg. 197 grams of distillate was condensed by the external condenser; 1156 grams of heel remained in the still. The distillate contained 52.1% L-lactide, 3.64% meso-lactide, 0.93% D-lactide and 2700 me/kg of acidity. On a 100% basis, the lactide
15 portion contained 91.9% L-, 6.4% meso- and 1.64% D-lactide.

Although a few exemplary embodiments of the present invention have been described above in detail, those skilled in the art will readily appreciate that the present invention embraces many combinations and variations other than those exemplified.

WHAT IS CLAIMED:

1. An improved process for depolymerizing an oligomer of an alpha-hydroxycarboxylic acid composition to a dimeric cyclic ester, the improvement comprising depolymerizing a thin liquid film of the oligomer at an effective depolymerization temperature and at a reduced pressure sufficiently low to vaporize the cyclic ester and form a vapor composition and collecting the resulting vapor composition.
2. The process of Claim 1 wherein (a) a molten oligomer is continuously fed to a reaction zone, and disposed as a thin film having a thickness of from about .05 to about 1.0 mm on an evaporation surface, whereby the oligomer comprising the film is depolymerized continuously and vaporized and the vapor is collected.
3. The process of Claim 2 wherein the feed rate of the oligomer to the reaction zone, the rate of disposing the thin film of the oligomer on the evaporation surface, the thickness of the film, the temperature and the pressure are coordinated and controlled such that the depolymerization proceeds substantially completely to form the vaporized composition containing the dimeric cyclic ester.
4. The process of Claim 1 wherein the depolymerization is effected in a thin film evaporator.
5. The process of Claim 4 wherein the evaporator is a wiped-film evaporator.
6. A process according to any one of Claims 1, 2, 3, 4 or 5 wherein the oligomer comprises an oligomer of lactic acid or an oligomerizable ester or nitrogen base salt thereof and the dimeric cyclic ester is a lactide.
7. The process of Claim 6 wherein the oligomer is an oligomer of lactic acid.

- 18 -

8. The process of Claim 2 wherein the evaporation surface of the heated reaction zone comprises the inner wall of a tubular reactor and the oligomer is spread as a thin film over the inner surface of the reactor.

5 9. The process of Claim 8 wherein the tubular reactor is a wiped film evaporator and the oligomer is wiped so that said oligomer forms a thin film having a substantially uniform thickness over the inner wall of the evaporator.

10. The process of Claim 1 further comprising:

1) providing a vertically disposed reactor having

10 (a) a substantially tubular reaction zone for depolymerizing said oligomer, the reaction zone comprising a substantially tubular evaporation surface having an upper region and a lower region,

(b) an oligomer feed means communicating with the upper region of the evaporator surface,

15 (c) an oligomer heel recovery means communicating with the lower region of the evaporation surface,

(d) a cyclic ester condensing means for condensing at least a portion of said vapor composition communicating with the evaporator surface, and;

20 (e) a wiping means contained within the tubular reaction zone adapted to spread the oligomer into a film over the evaporation surface,

2) maintaining the evaporation surface at said effective temperature and the reaction zone at said reduced pressure,

25 3) flowing liquid oligomer from said oligomer feed means and along the evaporation surface while wiping the oligomer with said wiping means so as to form a thin film over the evaporation surface,

4) condensing the resulting vapor composition containing the cyclic ester on the condensing means,

5) recovering unconverted oligomer from step(3) from the lower region of the evaporation surface, and;

30 6) recovering the cyclic ester from the condensate of step(4).

11. An apparatus for producing a dimeric cyclic ester comprising:

a first means for converting lactic acid to polylactic acid,

35 a second means connected to the first means for depolymerizing the polylactic acid to form a product comprising lactide, wherein said second means comprises a wiped-film evaporator,

- 19 -

a third means connected to the second means for extracting the lactide from the product, and;

a fourth means connected to the third means for precipitating the extracted lactide.

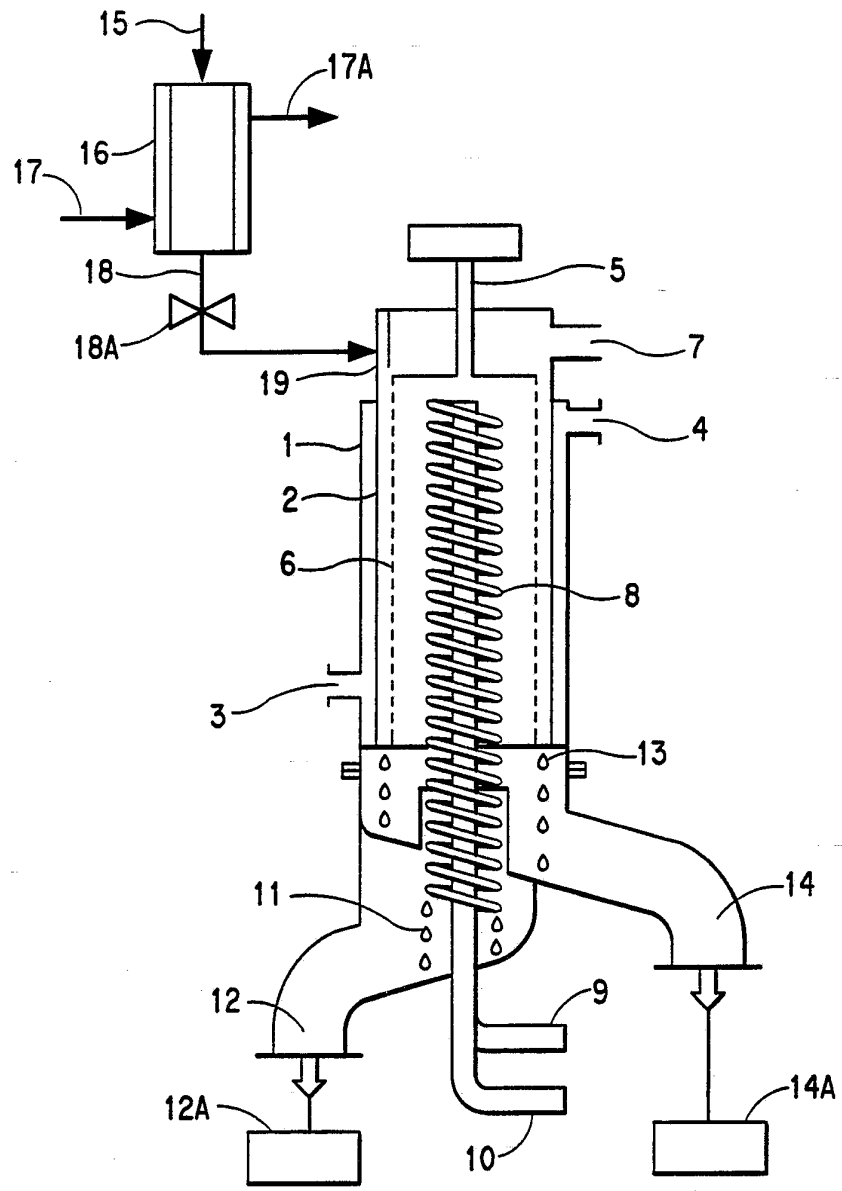
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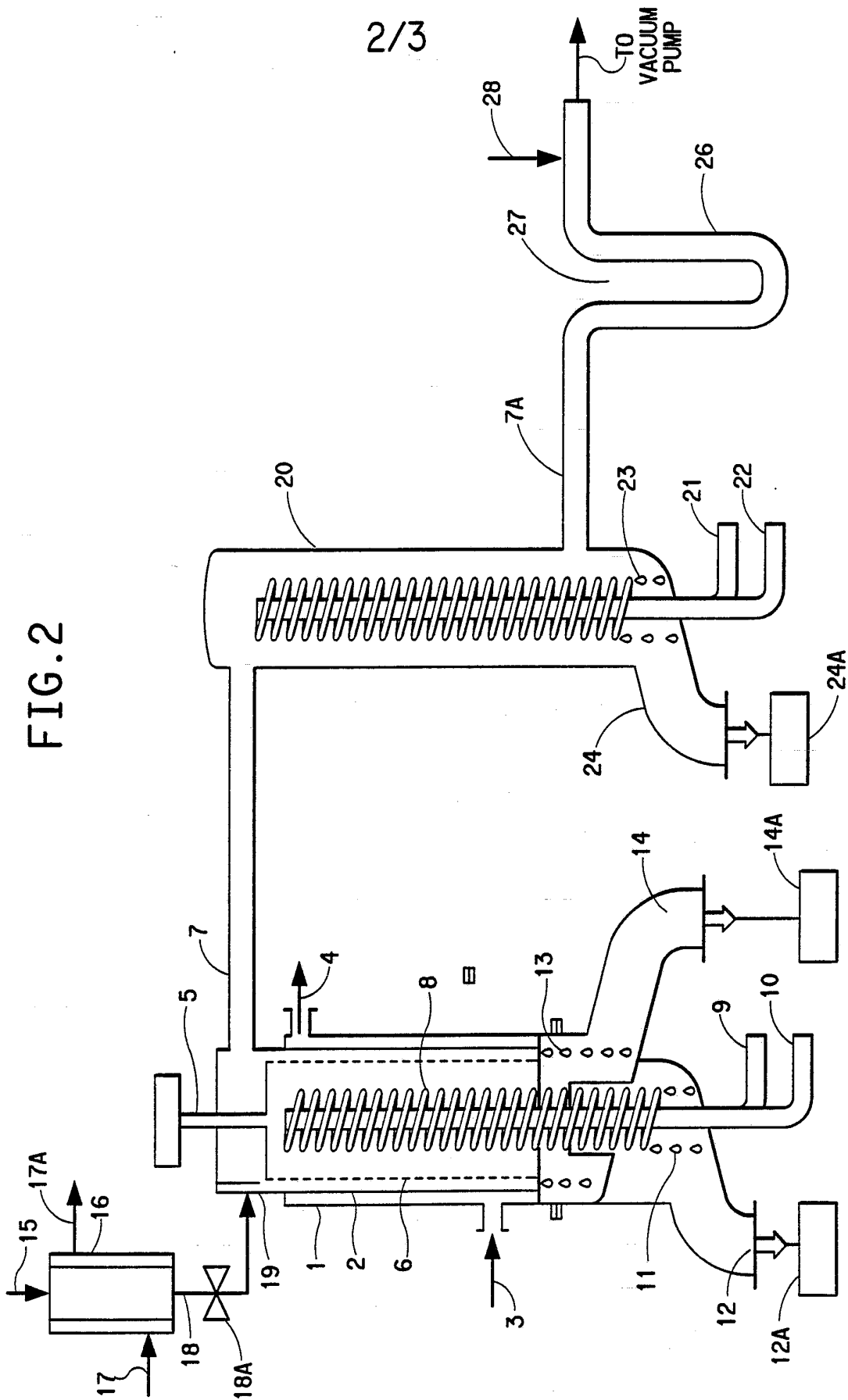
12. The apparatus of Claim 11, wherein the second means is connected to a hydrolyzer to convert residual polylactic acid to lactic acid.

10 13. The apparatus of Claim 12, wherein the hydrolyzer to connected to the first means in a manner sufficient to permit recycling the lactic acid from the hydrolyzer to the first means.

15 14. The apparatus of Claim 11, wherein the third means is connected to a concentrator in a manner sufficient to permit recovery of residual lactic acid from the third means in a form that is recycled to the first means.

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FIG. 1

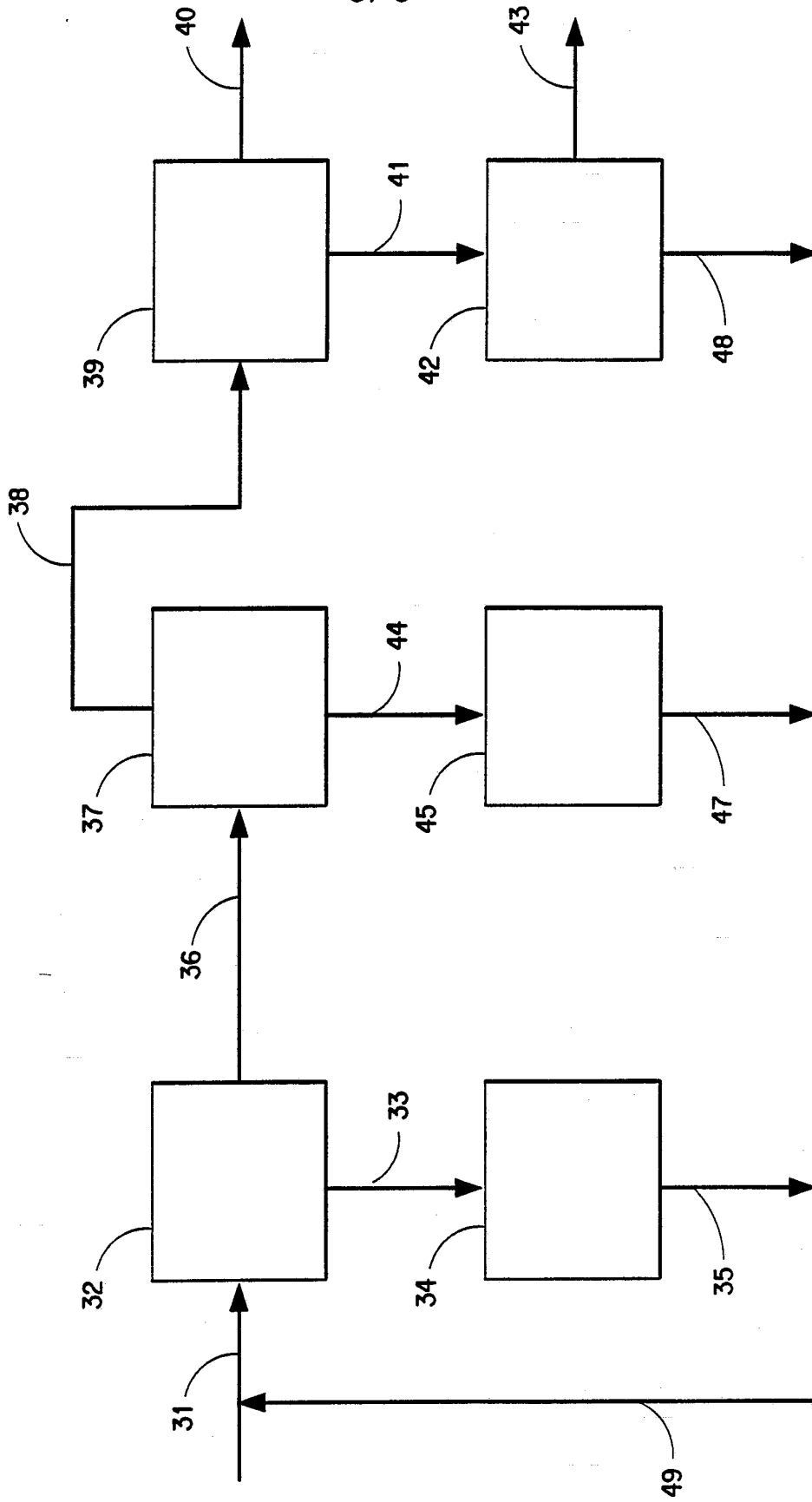




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FIG. 2

FIG. 3



INTERNATIONAL SEARCH REPORT

International Application

PCT/US 92/06003

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C07D319/12; B01J19/18		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C07D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ^o	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 5 023 349 (K.K. BHATIA) 11 June 1991 see column 1 - column 2 ---	1
<p>^o Special categories of cited documents :¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 16 SEPTEMBER 1992	Date of Mailing of this International Search Report 02. 10. 92	
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer RUSSELL F. ENGLISH	

ANNEX TO THE INTERNATIONAL SEARCH REPORT
 ON INTERNATIONAL PATENT APPLICATION NO. US 9206003
 SA 62632

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
 The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5023349	11-06-91	AU-A- 7762291	27-11-91
		WO-A- 9117155	14-11-91
		US-A- 5091544	25-02-92

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