PRODUCTION AND CURRENT APPLICATIONS OF BIODEGRADABLE POLYMER POLYLACTIDE (PLA) : A REVIEW

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ABSTRACT

Biodegradable polymer utilizes in various applications like natural packaging, paper coating, bio-plastics, films, bio-composites, in food processing and other disposable articles, as well as in biodegradable biomedical applications (tissue regeneration, implants and matrices for drug delivery devices). Aliphatic polyesters have tendency to biodegrade because ω-hydroxy-acids were obtained after enzymatic or hydrolytic cleavage, which in most cases are ultimately metabolized. Lactic acid has been an intermediate agent used in a wide range of industrial applications like food processing, cosmetics, pharmaceutical and biomedical. Lactic acid has received attention for use in a wide range of applications mostly as it acts as a monomer for the production of biodegradable poly (lactic acid) or polylactide (PLA). PLA can be produced chemically and biotechnologically but biotechnological routes are mostly favored because of environmental concerns and limited nature of petrochemical feedstocks. Worldwide efforts have been made for the production of lactic acid and PLA with good yield and low cost management. The details of raw material for lactic acid production, lactic acid producing microorganism, fermentation methodology, types of bioreactors used for the production of lactic acid, production yield of lactic acid, polymerization methods of PLA from lactic acid monomer and its recent application were discussed in this article.

Key Words: Biodegradable polymer; Polylactide polymer, Drug delivery, Microorganism, Raw material

INTRODUCTION

To overcome the problem of environmental pollution through outcome of automobiles, unused packing material, and one is the possible solution of these problems is to minimize the use or to enhance the reutilization of waste material. But simplest way to minimize the rate of pollution is by manufacturing article from biodegradable
material. Biodegradable material are those which can be biodegrade in the presence of environmental conditions like soil, moisture, microorganism, light, heat etc. and end products of this is not harmful to environmental. In today era Polylactides (PLA), which is a polymer of lactic acid, is widely use in different area of application. In this research article we are study about the production and application of PLA, which is a polymer of lactic acid monomer. A long history record of lactic acid used in fermentation, preservation of good stuffs is also available. Lactic acid was firstly discovered by Scheela in, 1780 in sour milk and named by Lavoisier is “acide lactique” in 1789 which became the origin of present terminology lactic acid. Lactic acid has been approved by the US FDA as GRAS (Generally Recognized as Safe) for the consumption of it as a food additive, cosmetic, pharmaceutical, medical implantation etc. It can be produced by chemically and biotechnologically both. But due to several serious problems, its biotechnology route is more favorable because racemic DL-lactic acid is produced by chemical synthesis from petro chemical sources whereas an optically pure L(+) or D(-) Lactic acid can be obtained by microbial fermentation of renewable sources and higher physical properties of polymerized poly (Lactic acid)(PLA) is crucially dependent on the optically pure L(+) or D(-) Lactic acid which is suitable for commercial products. A ray diagram is represented to explain all the route of lactic acid production.

For the pilot scale production of lactic acid though biotechnological route, there have been various requirement for high productivity i.e. cheap raw material, lactic acid producing microorganism, fermentation approach, type of bioreactor and finally purification of optically pure lactic acid for the production of high crystalline lactic acid.

So that production of PLA can be divided into two step i.e. production of Lactic acid and its Polymerization of PLA.

**Production of Lactic acid : Production of lactic acid can be divided into two steps :**

**Production of optically pure lactic acid isomer by fermentation of a carbohydrate source.**

**Raw material for lactic acid Production :**

For high productivity, low level contamination, high yield and for pilot scale production raw material should be cheap, easily available and easily purified after lactic acid production. Various readily available mono and disaccharide materials are generally used for its production like –

a) Glucose (dextrose) and glucose syrup as end product of starch conversion

b) Maltose as a product from Barley malt or other source

c) Sucrose as end product of beet and cane sugar production.

d) Lactose as a constituent of Whey

A list of raw materials and their microorganism are given in the Table 1 given below :
**Table 1: Raw Material and Microorganism for lactic acid production**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Raw material</th>
<th>Enzyme</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Corn starch</td>
<td>Lactobacillus amylophylus and L. amylovirus, Rhizophus oryzae</td>
<td>(7)</td>
</tr>
<tr>
<td>2.</td>
<td>Corn steep liquor (CSL)</td>
<td>Lactic Acid Bacteria (LAB) Lactobacillus Sp. RKY2 (KCTC 10353 BP)</td>
<td>(9) (7) (12)</td>
</tr>
<tr>
<td>3.</td>
<td>Corn Cob</td>
<td>Rhizophus oryzae</td>
<td>(7)</td>
</tr>
<tr>
<td>4.</td>
<td>Sucrose</td>
<td>Lactabaciillus delbreukii Subsp delbreuckii Lactobacillus lactis</td>
<td>(7)</td>
</tr>
<tr>
<td>5.</td>
<td>Lactose</td>
<td>L. delbreucii subsp. bulgaricus Lactobacillus helveticus</td>
<td>(7)</td>
</tr>
<tr>
<td>6.</td>
<td>Maltose</td>
<td>Lactobacillus helveticus</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Glucose</td>
<td>Lactabacillus Lactis, L. delbreukii Subsp. delbreukii (LDD; ATCC 9649)</td>
<td>(8)</td>
</tr>
<tr>
<td>8.</td>
<td>Molasses</td>
<td>Sporo lactobacillus cellulosolvens</td>
<td>(8)</td>
</tr>
<tr>
<td>9.</td>
<td>Whey</td>
<td></td>
<td>(9)</td>
</tr>
<tr>
<td>11.</td>
<td>Spent brewery yeast (Nitrogen source)</td>
<td></td>
<td>(9)</td>
</tr>
<tr>
<td>13.</td>
<td>Barley</td>
<td>Enterococcus faecalis RKY 1 Lactobacillus para casei 168</td>
<td>(10) (20)</td>
</tr>
<tr>
<td>14.</td>
<td>Wheat</td>
<td>Enterococcus faecalis RKY 1</td>
<td>(10)</td>
</tr>
<tr>
<td>15.</td>
<td>Corn</td>
<td>Enterococcus faecalis RKY 1</td>
<td>(10)</td>
</tr>
<tr>
<td>16.</td>
<td>Barley flour</td>
<td>Enterococcus faecalis RKY 1</td>
<td>(11)</td>
</tr>
<tr>
<td>17.</td>
<td>Cellulose</td>
<td>Lactobacillus casei subsp. rhamnosus</td>
<td>(11)</td>
</tr>
<tr>
<td>18.</td>
<td>Cellulose sapflour cellulose zein corn fiber corn fiber – soyflour Corn fiber – zein Corn – starch Corn starch – say flour Corn starch – zein Oat hull Oat hull soyflour Oat hull-zein</td>
<td>Lactobacillus casei subsp. rhamnosus Lactobacillus casei subsp. rhamnosus Lactobacillus casei subsp. rhamnosus Lactobacillus casei subsp. rhamnosus Lactobacillus casei subsp. rhamnosus Lactobacillus casei subsp. rhamnosus Lactobacillus casei subsp. rhamnosus</td>
<td>(12)</td>
</tr>
</tbody>
</table>
Microorganism of Lactic Acid Production:

The selection of an organism for fermentation is depends on the raw material to be fermented (carbohydrate). Different microorganism fermented different raw materials like sucrose, fructose, glucose, lactose starch etc. Acc. to Narayan et.al. Lactic Acid Bacteria (LAB) are the best microorganism for lactic acid production. Different variety of LAB should have different ability like L. delbreuckii subspecies delbreuckii ferment sucrose, L. delbreuckii subspecies bulgaricus ferment lactose, L. delbreuckii subspecies helveticus ferment lactose and galactose both, lactobacillus amylophilus and Lactobacillus amylovirus ferment starch, Lactobacillus lactis can use glucose, sucrose and galactose and lactobacillus pentosus detrorate sulfite waste liquor for lactic acid production etc. C. chan et.al. use lactobacillus delbreuckii subsp. delbreuckii (LDD) bacteria which appeared to require yeast.
extract above a certain critical level (< 2g/l). They also use some adsorbent PVP and activated carbon to prevent the inhibitory effect of product on reaction rate and to increase productivity. KiBeom Lee investigates in 2004 on different Industrial media for high yield and to reduce cost of nitrogen source. They fermented different composition of corn steep liquor, yeast extract and spent brewery yeast by Lactobacillus strain (LBM’s). These LBMS stains were, L. delbruckii sup lactis, L. casei, L. debrueckii (NRRL-B445), L. helveticus (NRRL-B1937) and L. casei (NRRL-B1922). Hurokoh et al. use Enterococcus faecalis RKY 1 bacteria for H. barley, H. wheat, M. corn, corn steep liquor fermentation to lactic acid. Ali Demrci et al. fermented pp composite (which is blended with various agricultural materials (like cellulose / Cellulose soy flour / cellulose Zein / corn fibre / corn fiber soy flour/ corn fibre flour/ corn fibre zein/ corn starch / corn starch soy flour/ corn starch Zein / oat hull / oat hull soy flour / oat hull zein/ soy hull / soy hull soy flour/ soy hill – zein) by Lactobacillus casei subsp. Rhamnosus. PP composite which is used as raw material is blended with cellulose / cellulose – soyflour, cellulose zein, corn fibre / cornfibre soy flour, corn fibre – Zien, corn starch, corn starch soyblour, corn stach .hull zein etc. Use of lactobacillus sp RKY2 for the fermentation of corn steep liquor was done by young Jung. Wee et al.

Mutation of strain Rhizopus oryzae RF 360 by means of nitrogen ion beam implantation to mutant strain R LC 41-6 which have high conversion rate to convert glucose into Lactic Acid. Lactobacillus pentosus can ferment the pre hydrolyzed liquor waste of trimming wastes of vine shoots into lactic acid. Sperolactobacillus cellulosolvent in continuous culture on molasses had maximum lactic acid productivities. Acc. to Gopal Reddy et al. Lactobacillus amylophilus GV 6 is an efficient and widely studied amylolytic lactic acid producing bacteria which is capable of utilizing carbon and nitrogen substances with high Lactic acid production efficiency. A.E. Ghaly et. al. investigated the effect of various conc. of different nutrients yeast extract and Lactomine AA on the growth of Lactobacillus helveticus and the production of lactic acid from cheese whey. Recently many researchers developed a mutant strain designated. Rhizopus Sp MK-96-1196 producing more than 90g/l L-lactic acid from Rhizopus Sp MK-96-1 by the ammonia – concentration gradient agar plate technique after mutation using N-methyl- N'-nitro-N-nitrosoguanidine (NTG) method. Some researcher optimize fermentation condition by optimizing all parameter like strain selection, phenotype, nutrient medium, pH, temperature etc. They optimized all these parameter on barley fermentation by Lactobacillus paracasei 168. W. Reimann studied on fermentation of glucose from hydrolysate of shredded barley and hydrolysate Rye. Some researchers find out a way for continuous lactic acid production system using an immobilized packed bed of Lactobacillus helveticus from cheese whey. To overcome the requirement of raw material for lactic acid production some alternative sources was investigated by S Schmidt et. al. Acc. to them Lactobacillus delbrucckii B445 can ferment waste paper as a cellulose feed stock. Some microbiologist has done batch and repeated batch production of L(+) lactic acid by Enterococcus faecalis RKY1 using wood hyrolyzate and corn sleep liquor. Moh. Altaf studied single step fermentation using starch substrate by L. amylophilus GV6.
Fermentation process and approaches of their production and purification:

Most frequently used procedures for lactic acid production are fed batch, batch, repeated batch and continuous fermentation. For the separation and purification many different procedures are used like through electrodialysis, reverse osmosis, liquid extraction through solvent, cell recycle via membrane, via ion exchange, through distillation, esterification etc. In fed batch fermentation when one batch fermentation was completed, the medium was replaced with a fresh medium to start new batch whereas in batch fermentation substrate added repetitively until the fermentation ceased to utilize the substrate or to produce the final product. In continuous production, separation of product is not stopped and the process of lactic acid production is run continuously. Ali Demirci et al. used mixed culture biofilm reactor for lactic acid production through continuous fermentation. In this firstly streptomyces viridosporus T7A (ATCC 39115) establish the biofilm and than L. casei subsp. rhamnosus produces lactic acid. Extractive lactic acid fermentation technique can give lactic acid yield of 0.99 kg/l and lactic acid productivity of 167 g/l/h over a conventional batch reactor which gave a yield of 0.83 g/l and lactic acid productivity of 0.31 g/l/h. A high volumetric productivity of 117 g/l/h using membrane cell recycle bioreactor is reported. Acetate was produced from whey lactose in fed batch and batch fermentation using co-immobilized cells of clostridium formico aceticum and lactococcus latis.

Downstream processing of the fermentation broth to obtain pure lactic acid

Under this we emphasis on recovery and purification of Lactic Acid. Lactic acid is a non boiling compound, is difficult to separate it from its solution. After fermentation a large amount of biomass and other solids also present in the broth.

A number of methods can be used for separation of lactic acid or lactate salt or its mix from the broth which are ion exchange separation, separation by adsorption, separation by vacuum distillation, by batch reactive distillation, by extraction, by solvent or by liquid-liquid extraction, precipitation of salt of cation with strong acid, electro dialysis, nanofiltration membranes coupled with ion exchange resin.

Ion exchange has been reported for extracting pure lactic acid from fermentation broth by ion exchange chromatography on a strongly acidic cation exchanger. Ion exchange combined with solvent extraction has been used for the recovery of pure lactic acid from a mixture of lactic acid, lactic acid salt and other solid biomass.

Electrodialysis is separation of lactic acid from its cell broth is recent. The E D stack was operated with five cell pairs of cation and anion exchange Neosepta membranes. Ki Lee has used electrodialysis for separation. He was used 80-100 g/L lactate as a feeding solution. Permeate and feed solutions were calculated with a flow rate of 1.68-1.72 L/min. In this study, electrodialysis was operated for 100 min with current of 8-12 A. C.C. Chen et. al. has developed coupled lactic acid fermentation and adsorption approach by using polyvinyl pyridine (PVP) and activated carbon as a adsorbent. These adsorbent can increase productivity and prevent product concentration from reaching inhibitory level by absorbing lactic acid and lactate. CaCO₃ is commonly added in fermentation broth to convert lactic acid in calcium lactate (Ca(La))₃. Liquid-liquid extraction or solvent extraction is an effective method but the fundamental requirement of a good solvent is a high distribution coefficient. In this, lactic acid
Acid can distribute between extractive solvent and aqueous solvent. Shigenobu et al. has been chosen different alcohol for esterification of ammonium lactate for the recovery of ammonia and free L-lactic acid. Rakesh Kumar et al. developed batch reactive distillation for lactic acid and also gave unsteady state mathematical model based on an equilibrium concept.

**Production of Poly Lactic Acid or Poly Lactide Polymer**

Lactic Acid is the building block for poly(lactic acid) and it has asymmetric carbon atom of exist in two optically active configuration L (+) Lactic acid and D (-) Lactic acid. In which Poly (lactic acid) can be prepared by polymerization of L(+)- lactic acid(30). The synthesis of PLA can follow two major routes. The first route is removal of water of condensation, which is removed by using a solvent under high vacuum and temperature. Poly (lactic acid) can produced by condensation polymerization is of low molecular weight, brittle, glassy polymer, which is unusable for any applications. The second route of producing PLA is to collect, purify and ring open polymerized lactic to yield high m.wt. PLA (35). In this process, water is removed directly from lactic acid, without using solvent, to produce a cyclic intermediate than dimer is purified under vacuum distillation and then “ring opening” polymerization is accomplished using heat, without solvent to produce polylactic acid6.

**Fig. 1** shows the synthesis pathway of route. Mitsui Toatsu Chemicals recently commercialized azeotropic dehydration process in refluxing, high boiling, aprotic solvent under reduced pressure to obtain high molecular weight PLA.

Youngiokim et al. has developed a procedure of preparation by ring opening polymerization by using Titanium Alkoxide catalyst. Lipase catalyzed polymerization of lactic acid developed by kondabagi R. Kiran et al.

**Fig. 2** : Different routes for PLA biosynthesis

**Characteristic of Polylactide Polymer :**

Poly lactic acid, a biodegradable poly hydroxy alkanoate (PHA), which is a promising replacement for synthetic Polymer. The advantages of Polylactic acid are its high tensile strength, high modulus, thermoplastic property, fabricability, biodegradability and bioenvironmental compatibility / absorbability. It is used in making of biodegradable sutures, clamps, bone plates and biologically active controlled release devices. PLA is degraded by simple hydrolysis of the ester bond without the presence of enzymes to catalyses this hydrolysis. The degradation rate of PLA is dependent on the size and shape of the article, the isomer ration and the temperature of hydrolysis.
The polymer should have adequate thermal stability to prevent degradation and maintain molecular weight. PLA undergoes thermal degradation at temp above 200°C. It can be degraded by lactic reformation, oxidative main chain scission, hydrolysis and inter or intramolecular trans esterification reactions\(^{40}\) oligomer, catalyst increase the degradation rate of PLA and minimizes the degradation temperature.

High molecular weight polylactic acid possess very good mechanical properties whereas when low m.w.t. Polyactic acid blended with other polymers, also exhibits characteristics of high molecular weight polymers\(^ {34} \). The amorphous PLA is soluble in organic solvent such as tetrahydro furan (THF), chlorinated solvents, benzene, acetonitrile and dioxane. High molecular weight PLA is glossy, stiff thermoplastic polymer. It can be crystallized by slow cooling, annealing it above the glass transition temperature. Degradation time of PLA is approx. six month to one year which is much lesser than the 500 to 1000 years for conventional plastics ex Polyethylene, Polystyrene\(^ {37} \).

**Current Uses and Applications of Lactic Acid and PLA :**

Lactic acid and its biodegradable polymer have received a significant amount of attention with many potential applications. Current uses and application of lactic acid can be classified into four major categories food, cosmetic, pharmaceutical and chemical application.

Lactic acid widely used in food industry because it is classified as GRAS for use as a food additive by the US FDA, Lactic acid as used commercially in meat and poultry industries, enhanced flavor, pH regulation, improved microbial quantity, mineral fortification. Due to the milk acid nature it is used as an acidulent in salads backed good, pickled vegetables and beverages. It is also used pH regulator food mix.

Lactic is also contributing major part in Pharmaceutical industry. Lactic acid is used in a wide range of mineral; preparation, which include prosthesis’s tablet, surgical sutures and controlled drug delivery system.

In cosmetic industry lactic acid used as pH regulators, anti acne agents, moisturizers etc. Nowadays lactic acid is most potential feed stock for chemical conversion because it contain two reactive groups carboxylic acid and hydroxyl group, due to which it act as a monomer for many use full chemical like acrylic acid, acetaldehyde, propanoic acid, dilactide, PLA etc.\(^ {41} \).

PLA acid exhibits many properties which make it suitable for use is medical devices, packaging, textile industries etc. It is equivalent or better than many petroleum-based plastics, which makes it suitable for a variety of application. It is clear and naturally glossy like the polystyrene used in “blist er packs” for products such as batteries, toys etc.\(^ {2} \). PLA is resistant to moisture and grease and also it have odor barrier and flavor barrier characteristics similar to polyethylene tere phthalate (PET) used for soft drinks and many other food products\(^ {42} \).

PLA have good tensile strength and modulus of elasticity like PET, PLA can be made with different mechanical properties suitable for specific manufacturing Processes, such as injection molding, sheet extension, blow-molding, thermoforming, film forming and fiber spinning using most conventional techniques and equipment\(^ {43} \).

Polylactic acid has much potential in the field of fibers and non woven. PLA can easily be convertible into a variety of fiber forms using conventional spinning processes. Spund bound and meltbound non wovens, continuous and stable fibers are all easily produced. PLA polymers are more hydrophilic than PET, have lower density
and have excellent crimp and crimp retention property. These polymers are stable to ultra violet light so that shows little fading towards light. PLA has low flammability and low smoke generation characteristic. Major application of PLA fiber and non wovens are not limited to clothing and furnishing such as drapes, upholstery and covers but it is also the major part of household and industrial wipes, diapers, feminine hygiene products, disposable garments and UV resistant fabrics for exterior use.44

PLA have major potential in the field of packaging Industries, because degradation of articles made by PLA is easier than plastics made articles. Four types of Polyaactic acid available for packaging purposes: PLA Polymer 4041D, 4031D, 1100 D and 2000 D. PLA polymer 4041D is “biaxially oriented” due to which it is stable upto temperature 255°F (130°C). It has excellent optical properties, good machinability and excellent twist and deadfold characteristics. PLA Polymer 4031 D is also a biaxially oriented film for high temperature application at 300°F or 150°C.Polymer 1100 D is a thermoplastic resin design for extrusion coating on paper and it is processes easily on conventional extension, coating equipment at a lower melt extrusion temperature than poly ethylene coatings. It is mainly used to lawn. Leaf bags, hot and cold drinking cups, picnic plates, bowls, straws, tried food boxes, frozen vegetable packaging and liquid food packaging.Polymer 2000D is a thermoplastic resin designed for extrusion and thermoforming application like food service ware, transparent food containers, blister packs and cold drink cups.44 Takashi et.al measured the basic electrical insulation characteristic of biodegradable PLA and they found that the volume resistivity, dielectric constant and dielectric loss tangent measured at room temperature were almost the same as those of cross linked polyethylene (XLPE). So that it can be used as insulating material for cables and electric wires.45

CONCLUSION

Polymer from renewable resources can be significantly lower in green house gas emission and fossil energy use today as compared with conventional and petrochemical based polymer. So to save our future and our environment, we should establish pilot scale production of Polylactide (PLA) and develop a technique of PLA production with low cost, so that we can commercialize it widely. The bright future will come only with significant investment of time, efforts and money.

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