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Case Studies on Synthesis of PLLA Bioplastic Starting from Food and Agricultural Wastes

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Abstract

Polylaevo Lactic Acid (PLLA) is an excellent biopolymer that is biodegradable and has characteristics exactly similar to polystyrene. However, at present, the market price of this biopolymer is significantly higher than polystyrene and other synthetic plastics. The major hindrances to the large scale manufacture of this polymer are the lack of availability of a cheap raw material and the overall economy of synthesis of lactic acid from the same. In this paper, the solutions to the above two bottlenecks are discussed based on the successful industrial projects handled by the author. The two recommended raw materials for the synthesis of PLLA are (1) cheese whey and (2) molasses. Both are discharged as waste effluents by industries, the former by dairy farms and milk processing units and the latter by sugar manufacturing units. In the case of cheese whey, it has to be first freed from proteins by ultrafiltration. A novel design of tubular ultrafiltration module developed by the author, that employs variable area tubes, provides much higher permeation rate and enhanced solute rejection. The protein concentrate obtained is of food grade and thus forms a valuable byproduct of the process. The cheese whey permeate/molasses is fermented to produce lactic acid in a continuous fluidized bed biofilm reactor, the former using a culture of Lactobacillus helveticus and the latter Enterococcus faecalis. The performance of the bioreactor has been simulated mathematically and a multi-parameter CAD (software) package has been developed. The package has been tested and verified using elaborate experimental data (collected both on laboratory scale as well as on pilot plant scale). Direct industrial adaptation of the developed CAD software can be thus recommended with confidence. Based on the above innovations, lactic acid can be economically synthesized on commercial scale starting from low cost natural materials and this would make industrial production of a biodegradable plastic such as PLLA substantially cost effective.

Keywords: *Bioplastics, PLLA, cheese whey, molasses, ultrafiltration, diverging-converging tubes, fluidized bed biofilm reactor, lactic acid synthesis, CAD software*

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INTRODUCTION

The family of biopolymers encompasses a wide horizon and this includes all the polymeric materials that occur in the nature such as:

1. All starches and polysaccharides
2. All proteins and protein derivatives
3. Wood, cellulose and cellulose derivatives
4. Natural rubber (obtained from rubber plantations or *Hevea* trees)

However, in an engineer's dictionary, bioplastics have a separate definition.

A material is called bioplastic only if it satisfies all of the following three characteristics simultaneously:

1. It must be a substance that is being used (or can be used) as a commercial material of construction. Accordingly, it is being manufactured (or is to be manufactured) in millions of tonnes per year all over the world.
2. It must be a substance that can be manufactured on large scale from naturally occurring raw materials. In other words, it must be photo synthetically renewable. The raw materials must be those that can be cultivated (in industrial plantations) as per requirement and henceforth, there should never be any uncertainty regarding their availability.
3. It must be biodegradable (degradable by soil bacteria). Thus, when disposed as waste to the soil, it gets degraded biochemically and becomes a constituent of the soil (often, fertilizes the soil).

Unless all of the above three conditions are simultaneously satisfied, the material under consideration cannot be labeled as a bioplastic. Against this background, the bioplastics that have made their entry to the technological world are[1],

(1) Natural rubber (polyisoprene)
(2) PHB (Poly-β-hydroxy butanoate)
(3) PLLA (Polylaevo lactic acid)

To be very precise, natural rubber is to be classified under the category of *elastomers.* It must also be noted that polyisoprene is being synthesized from petrochemical sources as well all over the world. Isoprene is a hydrocarbon that can synthesized from petroleum oil and this on polymerization yields polyisoprene (the characteristics of which are exactly similar to those of natural rubber). Since rubber pants (*Hevea brasiliensis*) cannot be cultivated in all types of soil and they grow little in cold climates, commercial synthesis of polyisoprene from petroleum sources has become popular in many parts of the world. In such a case, it cannot be labeled as a bioplastic or a biopolymer.

PHB, though has a striking resemblance to polypropylene and could make a viable substitute to PP, has the inherent drawback that it is an intracellular product. This polymer is synthesized by many microbes within their cells and to manufacture the same, we have to culture these microbes on very large scale. When the polymer is required to be produced in millions of tonnes per year, this shall form a herculean task. The present high market price of PHB (around 20 times that of polyethene (PP) is due to this. Microbes such as *Alcaligenes eutropha* synthesize PHB within their cell mass and are capable of accumulating PHB upto 90% of their dry weight. *Rhodobacter* accumulates PHB upto 80% of its dry weight, while *Azotobacter* and *Psuedomonas* accumulate PHB upto 73 and 63% of their dry weight respectively. After harvesting the cells, PHB can be separated from the cell mass by solvent extraction using methylene chloride as the solvent. In case of *Alcaligenes eutropha*, the dry cell mass may be used directly as bioplastic since it contains more than 90% PHB.

Attempts are being made to isolate the *PHA synthase* (Polyhydroxy alkanoates) enzyme from these microbes and then manufacture PHB in commercial bioreactors using this enzyme. Research projects in this connection have already been undertaken by the author and his coworkers. Until this is commercially successful, utilization of PHB shall remain restricted to special applications such as production of disposable syringes, wound dressings, cosmetic containers, fast food packaging films etc.

In the present scenario, the most promising commercial bioplastic is, therefore, PLLA (Poly Laevo Lactic Acid). Its characteristics are truly attractive:

1. The properties of PLLA are exactly similar to those of polystyrene (PS)

and it can be easily modified to make it similar to polyethene (PP) or polypropene (PP). Accordingly, it can be employed in all commercial or domestic applications where polystyrene, polyethene, polypropylene are presently employed. Its commercial acceptability is thus excellent.

2. PLLA melts at 170–180°C and its tensile strength is 70 MPa. It also has 94% transparency (unlike PS, PP or PE).
3. PLLA is a green plastic. Being biodegradable, its disposal as plastic waste shall not cause any environmental damage. This obviously is a distinct advantage over synthetic plastics.

MANUFACTURE OF PLLA BIOPLASTIC

Commercial manufacture of PLLA bioplastic involves two major steps:

1. Synthesis of polymer grade lactic acid from an economically available, natural raw material,
2. Polymerization of lactic acid to PLLA.

The second step is a well-established one as polymerization of lactic acid (once available in pure form) can be accomplished on commercial scale with the available technology. Lactic acid dimerizes easily at ordinary temperatures to form a solid cyclic dimer. This dimer can be then subjected to ring-opening polymerization to produce PLLA in a batch/continuous reactor.

The process is analogous to synthesis of polycaprolactum (Nylon-6) from caprolactum. The molten dimer is fed to the batch autoclave (operating at 200°C, 1 atm) where it polymerizes (the batch time ranges from 8–12 hrs) and molten polymer is discharged from the reactor using extrusion pumps, cooled first in a blast of nitrogen gas, then under water spray, cut into chips ,dried and sent to storage. Since Nylon-6 is the earliest polyamide fiber to be manufactured and is also the oldest man-made fiber, this is a popularly well-known process and the design of the polymerization reactor can be accomplished with relative case. The chief bottleneck lies in the first step. Till this date, most of the studies have been conducted (mostly on laboratory scale in test tubes / shake flasks) using aqueous solutions of cane sugar, glucose or corn starch as the substrate for fermentation to lactic acid. These substrates are extremely expensive for use as staring materials for the commercial synthesis of lactic acid. The market price of PLLA presently remaining prohibitively high is due to this lacuna. The most important requirements for the successful, economical synthesis PLLA bioplastic are, therefore, two-fold:

1. Identification of a cheap, easily available raw material for the production of lactic acid monomer,
2. Performance analysis and computer aided optimum design of an industrial bioreactor for conducting the fermentation process.

This paper discusses means of accomplishing these two requirements in the most optimum, cost effective manner and thereby proposes means of economical synthesis of PLLA bioplastic on commercial scale.

Raw Material Synthesis

The two most recommended raw materials for the production of polymer grade lactic acid by fermentation are,

1. Molasses
2. Cheese whey permeate

Molasses is the mother liquor left behind after the crystallization of sugar from sugar cane juice. It is an industrial effluent discharged by all cane sugar manufacturing units and is thus available practically free of cost. After preliminary

treatments such as filtration and clarification, molasses is diluted to a sucrose concentration of 50–150 g/L and then can be used as feedstock for lactic acid production by fermentation using a microbial culture of *Enterococcus faecalis.*

Cheese whey is the mother liquor left behind after the separation of casein from milk. This is also discharged as a waste effluent by all the dairy farms and milk processing units. Cheese whey does have high nutrient value since all the proteins, vitamins, lactose and minerals remain behind in the whey. The amount of whey produced per tonne of milk processed is also significantly large.

Cheese whey is to be first subjected to ultrafiltration to separate the proteins. Ultrafiltration, using treated polyamide membranes, is a cost effective process for protein separation since it does not consume any thermal energy and is capable of selectively separating practically all of the milk proteins. Since proteins are of high molecular weight, the trans-membrane pressure difference required to be maintained is low (3–7 atm). This minimizes the operating cost. The permeate leaving the UF unit that shall have an average lactose concentration of 30 g/L can be then used as the substrate (could be after dilution to 9-10 g/L lactose) for lactic acid synthesis by fermentation. The recommended microbial cultures are those of *Lactobacillus helveticus* and *Lactobacillus bulgaricus.*

In the case of conventional tubular UF units, the chief operating problems are those of concentration polarization and membrane clogging (or fouling). Due to concentration polarization or gel formation at the boundary (near the membrane surface), the permeate flux decreases significantly. An excellent solution to this bottleneck is the improved design of UF module proposed by the author[2]. This modified design utilizes tubes of diverging-converging geometry instead of straight, cylindrical geometry as shown in Figure 1. Each tubular membrane has a maximum diameter D_2 and a minimum diameter D_1 such that,

$$\tan(\theta) = (D_2 - D_1) / L_S = 1/12 \quad \text{Eq. (1)}$$

Or,

$$\theta = 5° \quad \text{Eq. (2)}$$

Where L_S is the segment length and θ is the angle of convergence/ divergence. It can be thus noted that the proposed geometry differs from straight, cylindrical geometry by not more than 5°.

The performance characteristics of the proposed design of UF module have been analyzed by the author[2] both mathematically as well as experimentally. A rigorous mathematical model has been developed that involves segment to segment analysis. The tubular module is assumed to be divided into a number of differential segments (each of length Δz), the concentrate from each segment being the feed solution to the next. The permeate flux from each segment is computed separately and the overall permeate delivery rate is then estimated by summation over the entire length. To note that the permeate rate varies from segment to segment not only due to change in concentration of the feed solution but also due to continuous change in cross sectional area of module in the axial direction. The values of permeate flux and solute rejection computed based on the above simulation model are compared with those determined experimentally (in a laboratory UF module) and satisfactory agreement has been observed between the two, the maximum deviation being 12.5%. The performance characteristics of the proposed design have been thus established both mathematically as well as experimentally.

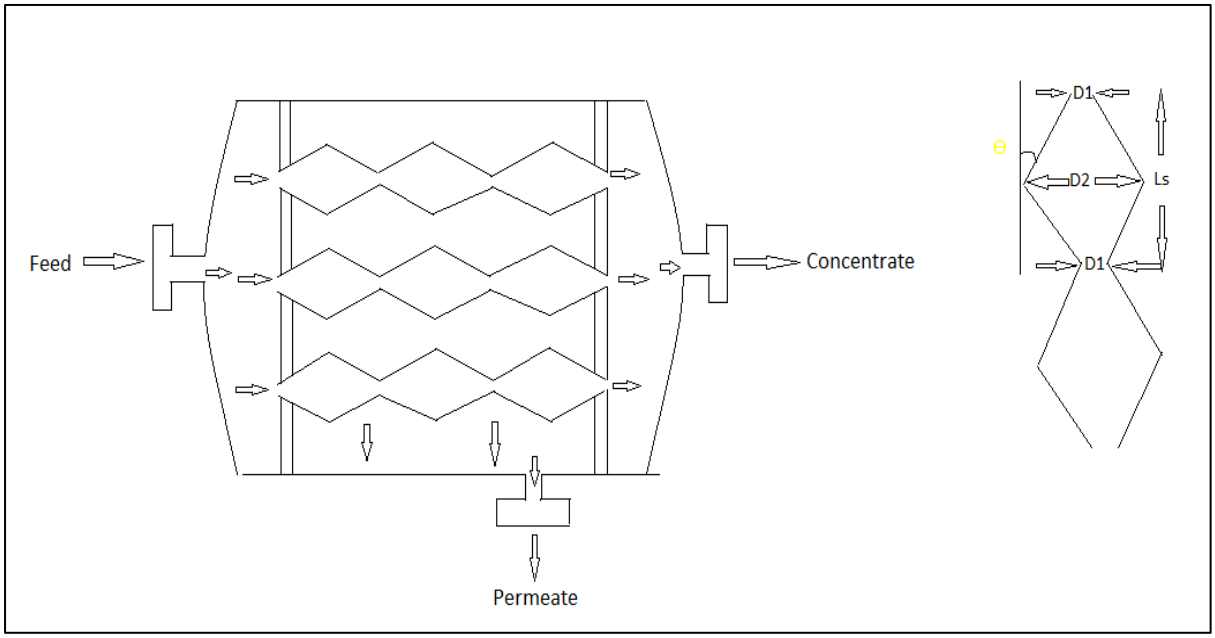

Fig. 1: *Schematic of Modified Design of UF Unit. θ = angle of convergence ≈ 5°.*

The attractive features of this design are-

1. It provides 400% (or four times) higher permeate flux as compared to a conventional tubular module of same membrane area per unit length,
2. The solute rejection provided by the module of proposed configuration is 1.5 to 1.6 times that in the equivalent straight tube module,
3. The frictional pressure drop in the proposed construction is only 1.15 to 1.18 times that in the conventional UF module of same membrane area per unit length, thereby illustrating that the operating cost of this module shall only be marginally higher than that of conventional design,
4. Scale deposition and consequent membrane fouling are at a lower degree in the module of proposed configuration (this must be due to the added turbulence provided by the constricted wall geometry and the consequent chances of re-entrainment of deposited dirt into the flowing fluid); this thus enhances the useful life of the membrane,
5. The protein concentrate obtained is of good quality containing little salt, lactic acid and lactose and there is hardly any denaturation of proteins.
6. The protein concentrate is thus of food-grade and forms a valuable byproduct of the process. The whey permeate may be then fed to the bioreactor without any further pretreatment.

Design and Analysis of Bioreactor (Development of Software Package)

Once economical raw materials for lactic acid synthesis have been identified (to note that both molasses and cheese whey are waste effluents discharged by process industries and thus do not demand any manufacturing cost), the second challenge is the optimum design of an industrial bioreactor. A well tested software has been developed by the author for the computer aided design of a fluidized bed biofilm reactor that can be effectively employed for the synthesis of polymer grade lactic acid from molasses / cheese whey permeate. The bioreactor consists of support particles made of silica (average

size = 2.5 mm) that are soaked in microbial solution (*Enterococcus faecalis* culture in the case of molasses and *Lactobacillus helveticus* in case of cheese whey permeate) so as to form a thin biofilm around each particle (the thickness of which remains more or less constant throughout the operation of the reactor).These particle-biofilm aggregates are fluidized and kept in suspension in the ascending stream of substrate solution (molasses or cheese whey permeate). As the solution moves up, the substrate (sucrose / lactose) diffuses into the biofilm where the biochemical reaction occurs.

The product (namely lactic acid) diffuses out and is carried upward in the ascending fluid stream. At the top of the reactor, the solution enters a disengagement zone of larger cross-section. Due to the increase in cross-sectional area, the fluid velocity decreases and any of the particles (particle-biofilm aggregates) that have got entrained in the fluid stream settle down back to the fluidized bed. The product solution is then discharged through the top outlet. The process is fully continuous, the substrate solution being fed from the bottom and the product solution being discharged continuously from the top. The particle-bio film aggregates remain inside the reactor, in the fluidized bed (reaction zone). If at all any microbial cells in the biofilm tend to decay, the dead cells immediately fall out and are replenished by fresh living cells. As a result, the biofilm thickness remains essentially uniform throughout the process. Due to the large biomass concentration in the biofilm (x_f = 100 to 200 g/L), the rate of bioconversion (rate of lactic acid production) shall be high in a bioreactor of this kind.

To simulate the performance of the bioreactor mathematically, it has been assumed to be equivalent to a plug flow dispersion reactor (PFDR). The performance of the reactor is thus in between that of an ideal continuous stirred tank reactor (CSTR) which operates with cent percent back mixing and an ideal plug flow reactor (PFR), which operates with zero back mixing. The bioreactor under consideration operates with a given degree of axial dispersion and this is governed by the magnitude of the axial dispersion coefficient (D_L). Accordingly, the performance equation of the reactor is,

$$-U_L(dC_S/dz) + D_L(d^2C_S/dz^2) = \eta(-r_S)(int) \quad \text{Eq. (3)}$$

Where,

$$U_L = Q_0 / (A\,\epsilon_f) \quad \text{Eq. (4)}$$

i.e., fluid velocity through the fluidized bed

Q_0 = volume flow rate (feed rate) of substrate solution

$$A = (\pi D^2 / 4) \quad \text{Eq. (5)}$$

Where A represents cross-sectional area of reactor column,

D = diameter of reactor column

ϵ_f = voidage (fractional liquid holdup) of fluidized bed

D_L = axial dispersion coefficient

η = effectiveness factor

$(-r_S)(int)$ = intrinsic rate of reaction (biosynthesis)

An experimental value of axial dispersion coefficient (D_L) is used in the computations. Kinetics of lactic acid synthesis from molasses using a culture of *Enterococcus faecalis* has been studied by Anjana and Kumar[3]. They have developed a Monod type kinetic equation for the process and have observed that substrate inhibition to microbial growth is negligible, though product inhibition does exist. However, they have considered suspended growth in a batch reactor. In a continuous flow process that is under consideration, there shall be little accumulation of lactic acid in the biofilm and product inhibition to microbial growth shall be insignificant. Also, as stated earlier, the biomass concentration in the biofilm remains more or less constant at x_f (the value of x_f ranging from 100 to

200 g/L). Consequently, the kinetic equation proposed by them is to be modified to make it applicable to the present system, as given below:

$$(-r_s)(int) = \mu_m(app)C_S/(K_S + C_S) \quad \text{Eq. (6)}$$

Where, $\mu_m(app) = (\mu_m/Y)x_f f(1-\epsilon_f)/\epsilon_f$ Eq. (7)

f = volume fraction of biofilm in the particle – biofilm aggregate

$$f = 1 - (d_p/d_{Pm})^3 \quad \text{Eq. (8)}$$

$$d_{Pm} = (d_p + 2\delta) \quad \text{Eq. (9)}$$

δ = biofilm thickness (assumed constant)

d_P = diameter of support particle

The values of kinetic constants reported by Anjana and Kumar[3] are, (μ_m/Y) = 3.33 hr $^{-1}$ and K_S = 0.1 g/L. These have been used in the present analysis.

To be precise, the expression for intrinsic rate as given in Eq. (6) is to be written in terms of C_{SP} which is the substrate concentration at the surface of the biofilm (at the biofilm-liquid interface). However, keeping in mind the large degree of turbulence that exists in the fluidized bed, it is assumed that the mass transfer resistance (resistance to substrate transfer) in the fluid bulk is negligible and therefore, $C_{SP} \approx C_S$.

In case of lactic acid synthesis from cheese whey permeate using a microbial culture of *Lactobacillus helveticus*, the same kinetic equation as that given in Eq. (6) could be employed, except that the numerical values of kinetic constants shall be different:

μ_m = 0.7 hr^{-1}, K_S = 0.22 g/L, Y= 0.65 Eq. (10)

The above values of kinetics constants are based on the study reported by Schepers and co-workers[4] as well as the kinetic studies performed by the author and coworkers.

The value of effectiveness factor (η) that accounts for the resistance to substrate transfer into the bio film depends on the size of support particle, bio film thickness, effective diffusivity (D_e) of substrate into the bio film, substrate concentration at liquid-biofilm interface (C_{SP}), as well as the kinetic parameter. It is estimated from the correlation proposed by Gottifreddi and Gonzo[5] which is reproduced below:

$$(1/\eta)^2 = (1/\eta_d)^2 + exp[6(\phi)^2/\{5(1+\beta)^2\} - (1/\eta_d)^2] \quad \text{Eq. (11)}$$

Where

$$\eta_d = \left(\sqrt{2}/\phi\right)[(1+\beta)/\beta]\{\beta - ln(1+\beta)\}^{1/2} \quad \text{Eq. (12)}$$

$$\phi = L^*[\mu_m(app)/D_e K_S]^{1/2} \quad \text{Eq. (13)}$$

$$\beta = \left(C_{Sp}/K_S\right) \approx (C_S/K_S) \quad \text{Eq. (14)}$$

L* = characteristic dimension

= (volume of biofilm) / (surface area of biofilm)

$$= (d_{Pm}^3 - d_P^3)/(6d_{Pm}^2) \quad \text{Eq. (15)}$$

D_e = effective diffusivity of substrate into biofilm.

The boundary conditions governing the system are,

BC 1: At z = 0,

$$(U_L C_{SO}) = U_L C_S(at\ z > 0) - D_L(dC_S/dz)(at\ z > 0) \quad \text{Eq. (16)}$$

BC 2: At z = L_f, $C_S = C_{Se}$ Eq. (17)

To solve the performance equation, Eq. (3), we need to specify the operating fluid velocity (U_L) and it is also necessary to estimate fractional liquid holdup (ϵ_f) in the expanded bed. As it is usual with fluidized beds, the operating superficial velocity of fluid is selected in such a way that it falls in between the minimum fluidization velocity (U_{mf}) and the terminal free settling velocity (V_t) of the particle-biofilm aggregates. An order of magnitude of U_{mf} is first estimated from the correlation proposed by Wen and Yu[6] as given below:

$Re_{mf} = \left[\frac{d_{Pm}U_{mf}\rho_f}{\mu_f}\right] = [(33.67^2) + 0.0408Ar_m]^2 - 33.67$ Eq. (18)

Where, Ar_m = modified Archimedes number

$= (d_{Pm})^3(\rho_{Sm} - \rho_f)g\rho_f/(\mu_f)^2$ Eq. (19)

ρ_{Sm} = density of particle-biofilm aggregate

$= \rho_S(1-f) + \rho_m f$ Eq. (20)

ρ_m = density of microbial solution

The terminal free settling velocity (V_t) of particle-biofilm aggregate is computed from the generalized settling law through an iterative procedure:

$V_t = [4(\rho_{Sm} - \rho_f)gd_{Pm}/(3f_D\rho_f)]^{1/2}$ Eq. (21)

Where f_D is the drag coefficient, the value of which depends on the particle Reynolds number, Re_P :

$Re_P = (d_{Pm}V_t\,\rho_f/\mu_f)$ Eq. (22)

A value of V_t is first assumed. The particle Reynolds number (Re_P) is then evaluated from Eq. (22) and the value of drag coefficient (f_D) is retrieved from the standard f_D versus Re_P plot[7]. The terminal free settling velocity (V_t) is now computed from Eq. (21) and it is checked whether its magnitude agrees with that assumed at the outset. If not, computations are repeated using the newly computed value of V_t. The ultimate value of V_t is thus finalized by trial. The operating superficial velocity of the fluid, U (sup), is now selected such that

$1.5U_{mf} \leq U(sup) \leq 0.7V_t$ Eq. (23)

Since Q_0 = AU (sup), the value of operating fluid velocity (U_L) is obtained from Eq. (4).

The fractional liquid holdup (ϵ_f) in the expanded bed is estimated from the modified form of Richardson and Zaki's correlation proposed by Al- Dibouni and Garside[8]:

$\epsilon_f = [U(\text{sup})/V_t]^{1/n}$ Eq. (24)

Where,

$n = (5.1 + 2.7B)/(B+1)$ Eq. (25)

$B = 0.1\,(Re_P)^{0.9}$ Eq. (26)

The performance equation, Eq. (3) is solved numerically (after substituting expression for intrinsic rate from Eqs. 6–9 in it) subject to the boundary conditions BC-1 and BC-2 by a modified form of fourth order Runge-Kutta method. Computations were started from the top of the column (namely, reactor outlet) where $C_S = C_{Se}$ and proceeded downward until BC-1 is satisfied (where $z = L_f$). In other words, in the numerical algorithm employed, $z = 0$ corresponds to BC-2 (reactor outlet) and $z = L_f$ stands for reactor inlet (where BC-1 is to be satisfied). The algorithm has been observed to be quite stable and it is re-executed at different values of system / operating parameters such as the substrate flow rate (Q_0), fractional substrate conversion desired (α) and the biomass concentration in the biofilm (x_f).The results are illustrated graphically in Figures 3–6.

MATERIALS AND METHODS

Experiments were conducted using,

1. A laboratory fluidized bed column, 0.5 m in diameter
2. A pilot plant bioreactor, 1.0 m in diameter.

Silica particles of average size 2.5 mm were used as support particles in both reactors. Molasses and cheese whey are collected from two sugar manufacturing units and three milk processing units. Microbial culture used is that of *Enterococcus faecalis* in case of molasses and *Lactobacillus helveticus* for cheese whey permeate. Molasses (after filtration and clarification) diluted to a sucrose concentration of 50 g/L and cheese whey permeate with a lactose concentration of 9.0 g/L are fed from the bottom. The sucrose / lactose content of the product solution are measured using a

spectrophotometer at 600 nm wavelength and also by using HPLC (high precision liquid chromatograph). Each experimental run is repeated at least thrice (at each substrate flow rate) to ascertain experimental accuracy.

The comparison between computed values (estimated from the developed simulation model) and the experimental values of reactor height is illustrated in Figure. 2. Out of the 25–30 data points compiled, a few selected (illustrative) ones are shown only in the figure.

RESULTS AND DISCUSSION

It can be seen from Figure 2 that there is good agreement between the computed values of reactor height (L_f) and the experimentally determined values, the maximum deviation being 12.5%. This confirms the accuracy of the simulation model (CAD package) developed. The developed CAD (software) package can be therefore recommended for use in industrial practices (for the design of bioreactors, for the commercial synthesis of lactic acid from molasses or cheese whey permeate).

From Figures 3 and 4, it can be seen that the fractional conversion attained (α) decreases with increase in substrate flow rate (Q_0). Figure 3 is for molasses feedstock (biomass concentration in biofilm = 250 g/L, substrate (sucrose) concentration in raw feed = 50 g/L), while Figure 4 is based on data computed using cheese whey permeate as the feedstock (lactose concentration in raw permeate = 9.0 g/L, biomass concentration in biofilm = 150 g/L). The observation is not surprising since when the reactor volume is kept constant (reactor height = 3.0 m and reactor diameter = 0.5 m), lesser degree of substrate conversion can only be achieved at higher substrate flow rates.

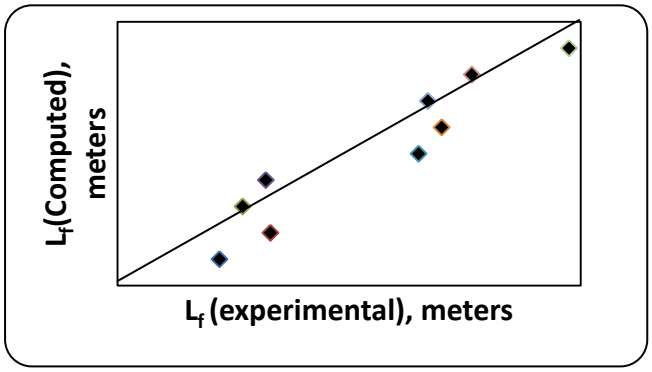

Fig. 2: *Comparison between Computed and Experimental Values of Reactor Height.*

This is further demonstrated in Figures 5 and 6 which depict the variation of reactor height (L_f) with feed flow rate (Q_0) at a specific value of fractional conversion (here, α = 0.80). Figure 5 considers fermentation of molasses and Figure (6) that of cheese whey permeate. Substrate concentrations in the feed solutions are same as before such as 50 g/L of sucrose for molasses and 9.0 g/L of lactose for cheese whey permeate. The reactor diameter = 0.5 m. From these figures, it can also be observed that the required volume of the fluidized bed increases when the feed flow rate (and thereby, the capacity of the bioreactor) increases. The increase, however, is relatively sluggish indicating that the reactor volume

requirement for attaining a large fractional conversion (a large production rate of lactic acid) is not substantial. This further speaks of the cost efficiency of the process.

The author and his coworkers[9,10] have also developed design of a diverging-converging fluidized bed bioreactor that provides 25–29% increase in the fractional conversion of sucrose / lactose as compared to the above straight column bioreactor of the same bed height and operating at the same feed flow rate. The performance features of this improved design of bioreactor (of diverging-converging geometry) have also been simulated mathematically and verified experimentally[10].

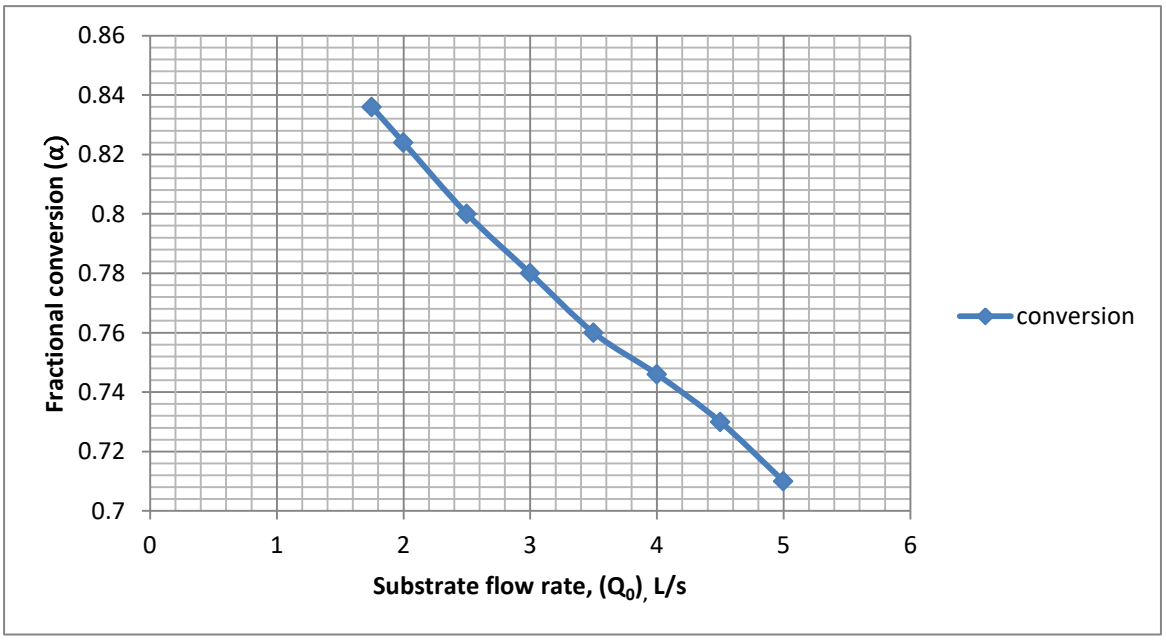

Fig. 3: *Variation of Fractional Conversion of Substrate with Substrate Flow Rate. Feedstock: Molasses, C_{S0} = 50 g/L, x_f = 250 g/L , L_f = 3.0 m.*

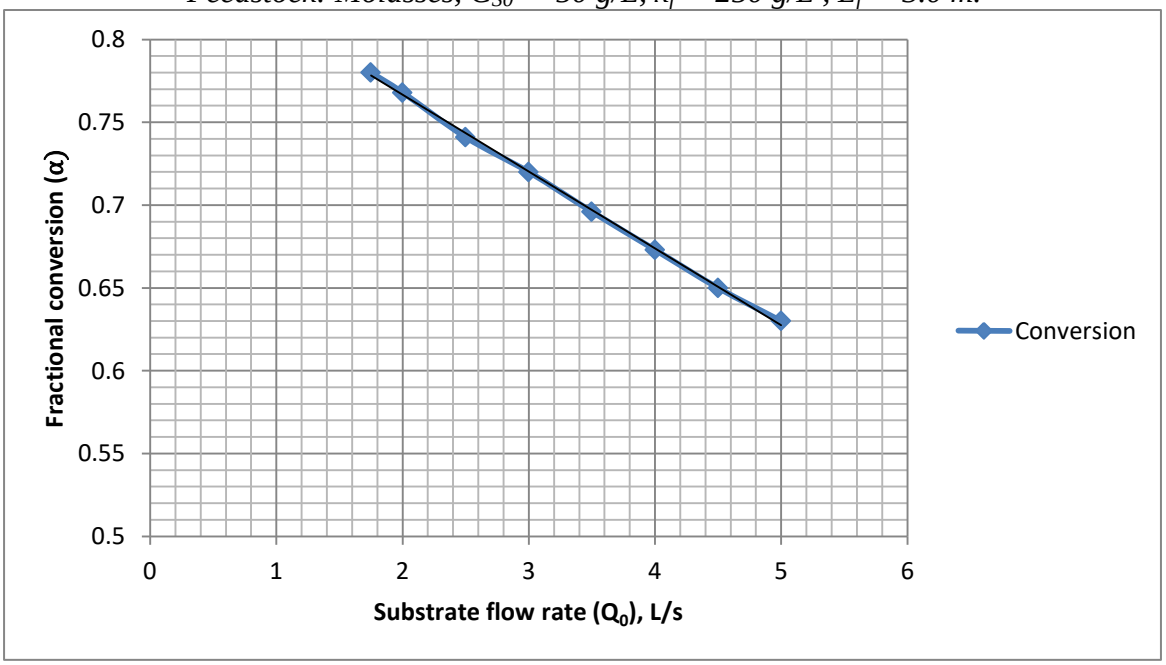

Fig. 4: *Variation of Fractional Conversion of Substrate with Substrate Flow Rate. Feedstock: Cheese whey permeate, C_{S0} = 9.0 g/L, x_f = 150 g/L , L_f = 3.0 m.*

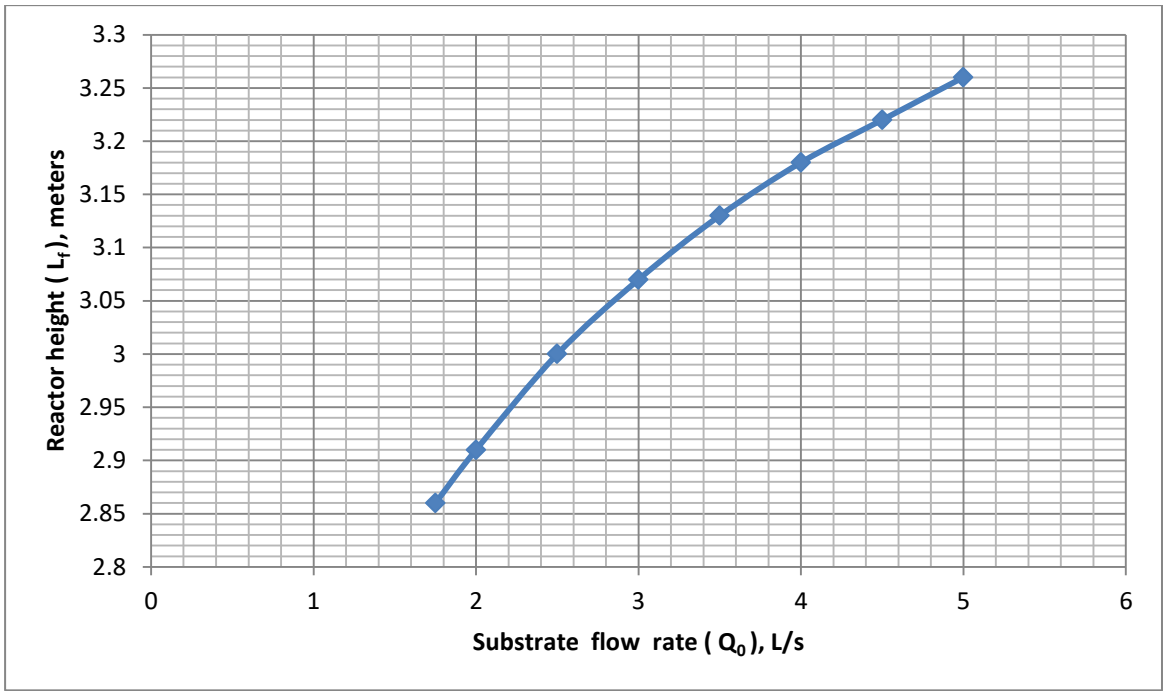

Fig. 5: *Variation of Reactor Height with Substrate Flow Rate.Feedstock: Molasses, C_{S0} = 50 g/L, x_f = 250 g/L, α = 0.80.*

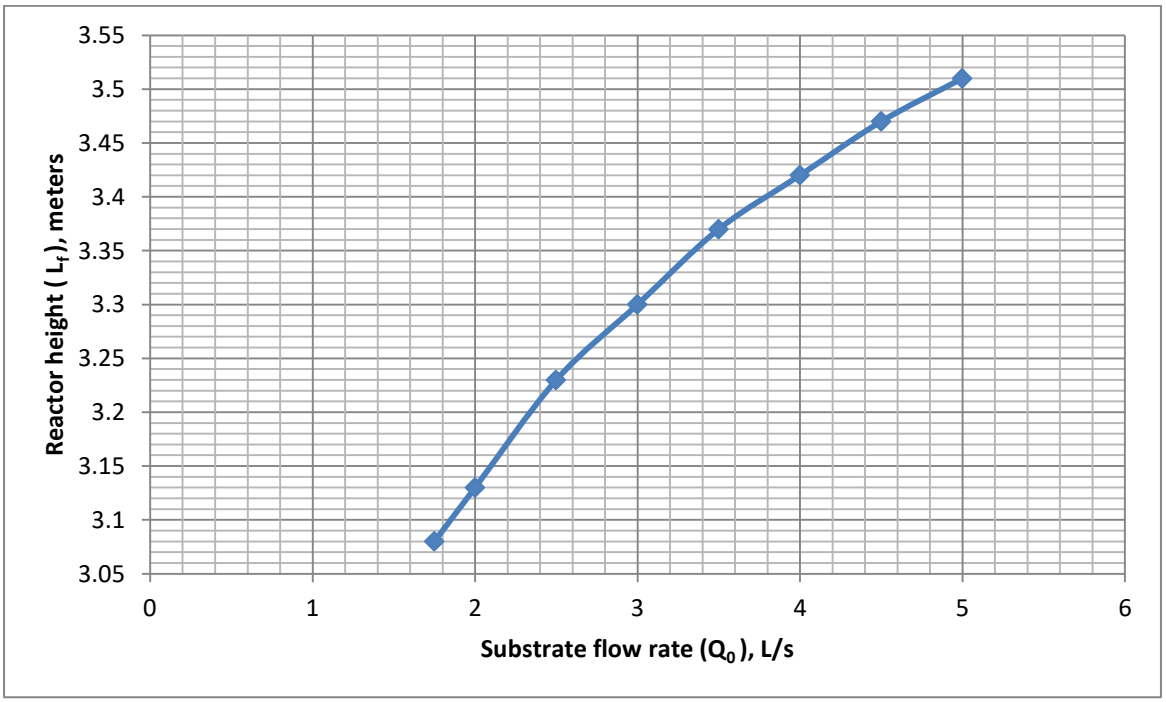

Fig. 6: *Variation of Reactor Height with Substrate Flow Rate.Feedstock: Cheese whey permeate, C_{S0} = 9.0 g/L, x_f = 150 g/L, α = 0.80.*

CONCLUSIONS

1. Economical raw materials for commercial synthesis of PLLA bioplastic have been identified such as, (a) cheese whey and (b) molasses. Both of these are effluents discharged by process industries and thus demand no manufacturing cost.

2. Food grade protein concentrate is obtained from cheese whey using improved design of tubular ultrafiltration (UF) unit which forms a valuable by product of the process.
3. The proposed design of UF unit that employs diverging- converging tubes made of treated polyamide (instead of straight, cylindrical tubes) provides enhanced permeate rate and much higher solute rejection ,with negligible increase in operating cost. The module also has much lower tendency to foul, thereby providing prolonged membrane life as well.
4. Versatile CAD software has been developed for the commercial synthesis of lactic acid from molasses / cheese whey permeate in a continuous fluidized bed biofilm reactor. The applicability of the CAD package has been tested and verified using elaborate experimental data collected on laboratory scale as well as on pilot plant scale.
5. The developed software can be thus employed with confidence for the design and installation of industrial fluidized bed bioreactors for the economical synthesis of lactic acid.
6. This shall permit commercial manufacture of PLLA bioplastic on a cost- effective basis and accordingly, its market price shall diminish and become comparable with that of other synthetic plastics such as polystyrene and polypropylene (which is the need of the day).

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NOMENCLATURE

A = area of cross section of bioreactor, m^2

Ar_m = modified Archimedes number, dimensionless

C_S = substrate concentration, g/L

C_{Se} = substrate concentration in product solution, g/L

C_{S0} = substrate concentration in feed, g/L

C_{SP} = substrate concentration at liquid-bio film interface, g/L

d_p = diameter of support particle, m

d_{pm} = diameter of particle-biofilm aggregate, m

D = diameter of fluidized bed biofilm reactor, m

D_1 , D_2 = minimum diameter and maximum diameter respectively of modified UF unit, m

D_e = effective diffusivity of substrate into biofilm, m^2 /s

D_L = axial dispersion coefficient, m^2 /s

f = volume fraction of biofilm in particle – biofilm aggregate, dimensionless

f_D = drag coefficient, dimensionless

K_S = kinetic constant, g/L

$L*$ = characteristic length, m

L_f = height of fluidized bed, m

L_S = segment length of diverging-converging tube of UF unit, m

Q_0 = volume flow rate of substrate solution, m^3/s

$(-r_s)(int)$ = intrinsic rate of reaction, g/(L.s)

Re_{mf} = Reynolds number at incipient fluidization, dimensionless.

Re_p= particle Reynolds number, dimensionless.

$U(sup)$ = superficial operating velocity of feed solution, m/s

U_L = velocity of fluid through the fluidized bed, m/s

U_{mf} = minimum fluidization velocity, m/s

V_t = terminal free settling velocity of particle- biofilm aggregate, m/s

x_f = biomass concentration in biofilm, g/L

Y = overall yield coefficient for cell mass production, dimensionless.

α = fractional conversion of substrate, dimensionless.

β = parameter defined in Eq. (14), dimensionless.

δ = biofilm thickness, m

ϵ_f = voidage of (fractional liquid holdup in) fluidized bed, dimensionless.
η = effectiveness factor, dimensionless.
η_d = parameter defined in equation (12).
θ = angle of convergence/ divergence, degrees
μ_f = viscosity of substrate solution, kg/(m.s)
μ_m = kinetic constant, s^{-1}
ρ_f = density of substrate solution, kg/m^3
ρ_m = density of microbial solution, kg/m^3
ρ_S = density of support particle, kg/m^3
ρ_{Sm} = density of particle–biofilm aggregate, kg/m^3
ϕ = Thiele-type modulus (defined in equation - 13), dimensionless.

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