POLYLACTIC ACID
THE GREEN PLASTIC

In recent years, the growing concern over environmental sustainability has driven significant interest in the development and adoption of green plastics. Among these, polylactic acid (PLA) has emerged as a promising alternative to traditional petroleum-based plastics. PLA is a biodegradable thermoplastic derived from renewable resources such as corn starch, sugarcane, and other biomass. Its production and use offer a myriad of environmental benefits, including reduced carbon footprint and decreased dependency on fossil fuels.

Polylactic acid stands out not only for its eco-friendly origins but also for its versatility and applicability across various industries. It can be used in packaging, agriculture, biomedical devices such as sutures and 3D printing.

The adoption of PLA as a green plastic is supported by its favourable properties, such as high mechanical strength, clarity, and compostability under industrial conditions. These characteristics make PLA particularly attractive for applications where both performance and environmental impact are critical considerations. As the global demand for sustainable materials continues to rise, PLA represents a significant step forward in the transition towards a more sustainable and circular economy.

While PLA can be considered an eco-friendly biomaterial with excellent properties, it also has many obvious drawbacks when confronted with requirements for certain applications:

1) Its degradation rate through hydrolysis of the backbone ester groups is slow and can sometimes take several years, which can limit its biomedical and food packaging applications.

2) PLA is very brittle and thus not suitable for demanding mechanical performance applications unless it is suitably modified.

3) PLA is permeable to gases and its wider industrial application is limited which prevents its complete access to industrial sectors such as packaging.

4) PLA is expensive relative to non-degradable plastics manufactured with feedstock from the petrochemical industry.

Figure 1 – Some uses of PLA aside from biomedical uses.

1. **Fermentation Dominance**: Over 90% of lactic acid production globally is achieved through the fermentation of carbohydrates derived from renewable resources like corn starch, sugarcane, and other biomass. This method is favoured for its sustainability, lower environmental impact and alignment with the circular economy principles.

   The biological fermentation route uses carbohydrates as substrates to produce lactic acid (LA) through microbial fermentation. Highly pure LA can be produced by a broad range of microorganisms, such as bacteria, fungi, algae and cyanobacteria. Furthermore, many low-cost biomass wastes, such as kitchen waste, straw and sludge contain a large number of degradable substances which can be used as substrates for the production of LA by biological fermentation. Currently, more than 90 % of LA in the world is produced by biological fermentation.

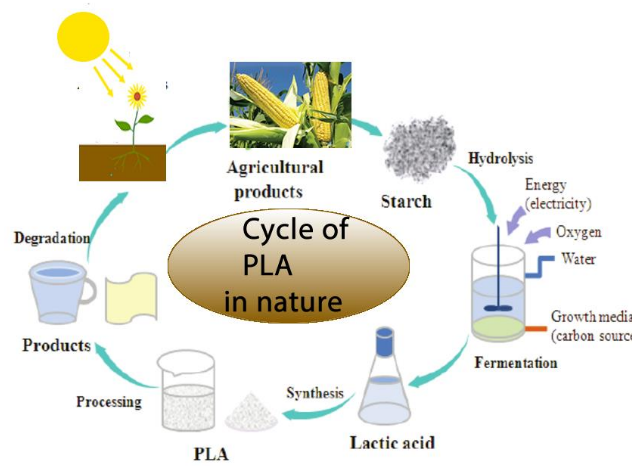


Figure 2 – PLA cycle via fermentation

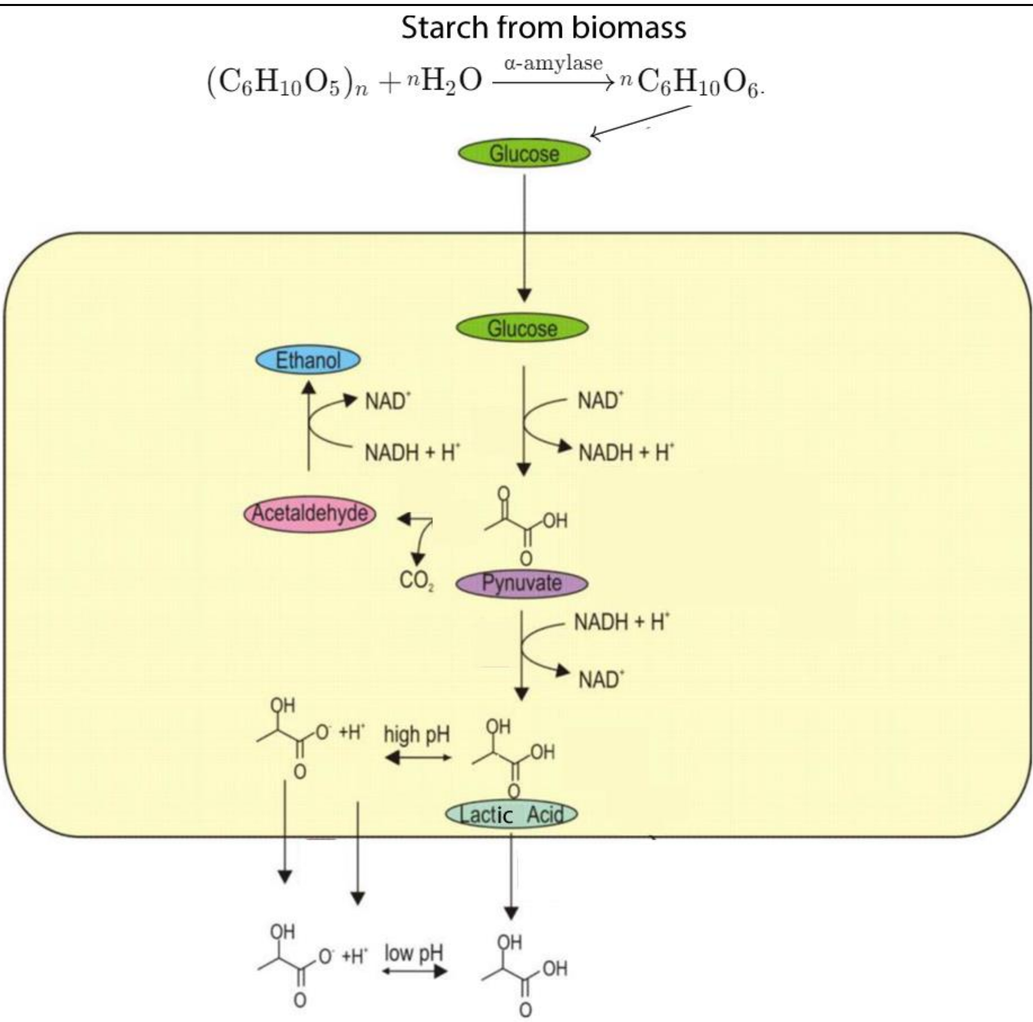


Figure 3 - fermentation pathway for the synthesis of lactic acid.

1. **Petrochemical Production**: The remaining 10%, comes from petrochemical sources. This method involves chemical synthesis from petrochemical derivatives such as acetaldehyde, which is converted to lactic acid through various chemical processes (fig 4). However, this method is less common due to concerns about the environmental impact and sustainability of using fossil fuels.

   The pathway to the chemical production of polylactic acid (PLA) is shown below in fig 4. Ethene, from the petrochemical industry, provides the feedstock for the process. This accounts for only 10% of the lactic acid used in industry to produce reusable and biodegradable plastics.

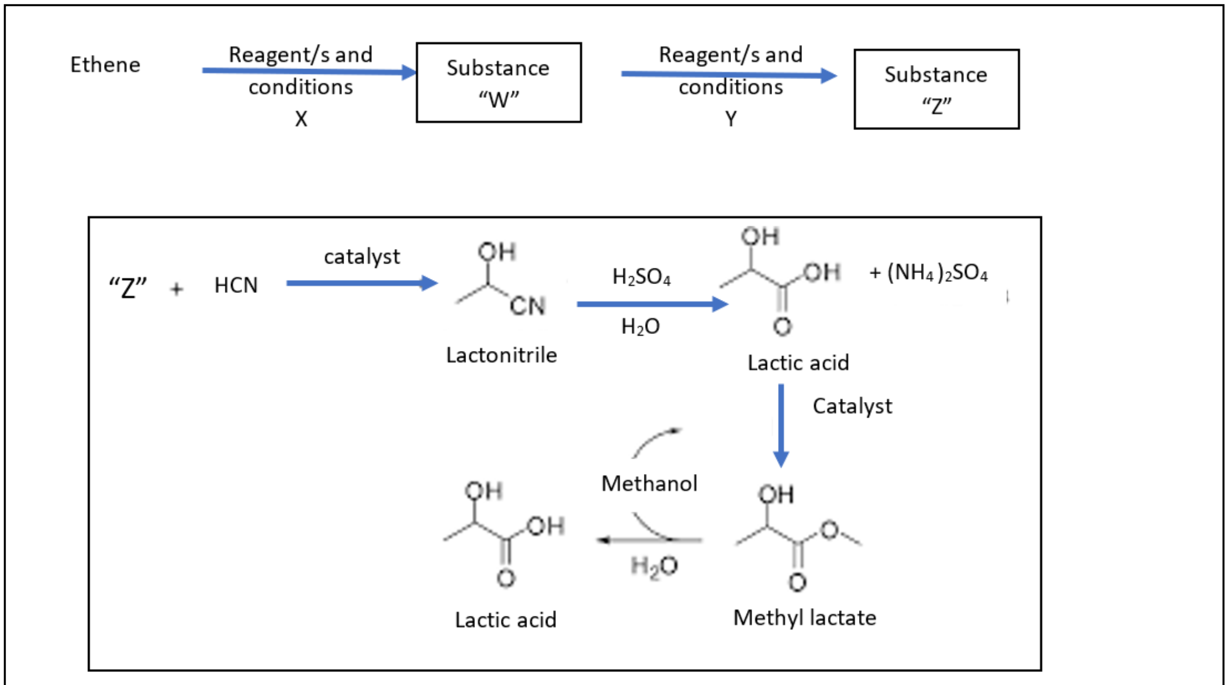


Figure 4 – Pathway for the chemical synthesis of lactic acid.

Fractional distillation, under reduced pressure, is used to separate lactic acid from impurities such as residual hydrogen cyanide and lactonitrile, both extremely toxic and to harmful to aquatic life. The BP of lactic acid is around 216 °C, however, at this high temperature the molecule starts to decompose thus reducing the overall yield. Under reduced pressure (vacuum), the boiling points of lactic acid is significantly lowered. For example, lactic acid boils at about 122°C at 15 mmHg, much lower than it would under atmospheric pressure. Fractional distillation is ultimately used to concentrate and purify the lactic acid.

1. Consider the reaction shown in fig 5.

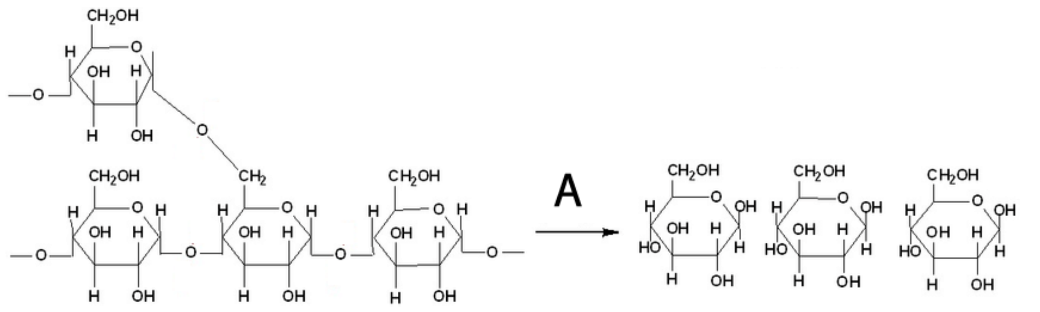


Figure 5 – enzymatic digestion of starch.

a. Name the reactant molecule.

______________*amylopectin (from the data booklet)*______________ ***1 mark***

b. Name the type of reaction that formed the reactant molecule.

________________*condensation polymerisation*________________
1 mark

c. Name the product molecule.

_____________ ***α****-D-glucose_(from the data book*)_________________ ***1 mark***

d. Name the type of reaction.

_________________*hydrolysis*________________ ***1 mark***

e. "A" represents a biological catalyst known as **α-amylase.** Alpha amylase works to cleave molecules from the ends of the molecular chains. A particular biomass (X) contains starch composed of 80% amylose and 20% amylopectin whilst another type of biomass (Y) contains starch composed of 70% amylopectin and 30% amylose.

i. Biomass X and Y were exposed to **α-amylase** under exactly the same temperature and pH. Which biomass will yield product at the fastest rate? Explain

Biomass Y has a higher percentage of the branched starch amylopectin. ----- 1 mark
The enzyme will cleave from the ends of each branch. More branching more cleaving per unit time hence grater rate of reaction -------- 1 mark

ii. A student suggested that increasing the temperature of the reaction vessel to 55 ^{o}C, in which reaction A takes place, will cause a greater rate of product formation to occur as the average kinetic energy of all reactant particles is increased.

Is the student right? ______*No*___ ***1 mark***

Give a detailed explanation, with reference to bonding and structure, to justify your response.
Enzymes are proteins that work via specific shaped surface sites called "active site".
The active site is part of the tertiary structure of the enzyme ------- 1 mark
held together by all typed of bonding namely H-bonding, covalent, ionic, dipole-dipole and dispersion forces. ---- 1 mark
These forces apart from the covalent bonds are relatively weak and break at low temperatures above 40 ^{o}C thus disrupting the tertiary structure and changing the shape of the active site. ---- 1 mark

2. Synthesis of lactic acid from biomass is preferred over synthesis of lactic acid via ethene. Identify and explain three green chemistry principles that support this preference, detailing how each principle is applied.

1. Use of Renewable Feedstocks ------ 1 mark

- ***Application****: Biomass, such as corn or sugarcane, is a renewable resource that can be replenished through natural processes or agricultural practices. ---- 1 mark*
  In contrast, ethene is derived from fossil fuels, which are non-renewable and take millions of years to form. ---- 1 mark

2. Design for Energy Efficiency ---- 1 mark

- ***Application****: The fermentation process used to produce lactic acid from biomass typically occurs under milder conditions (ambient temperature and pressure) ---- 1 mark*
  Compared to the high-energy requirements of petrochemical processes. Synthesis from ethene involves energy-intensive steps, including the cracking of hydrocarbons and subsequent chemical reactions under high temperature and pressure. ***----- 1 mark***

3. Reduction of Hazardous Chemicals ----- 1 mark

- ***Application****: Biomass fermentation to produce lactic acid is a relatively benign process, often using water as a solvent and producing non-toxic byproducts such as carbon dioxide and water. ----- 1 mark*
- *In contrast, petrochemical processes for ethene can involve hazardous reagents and byproducts, including toxic chemicals and greenhouse gases. ----- 1 mark*

Any other green chemistry principle that can be justified is accepted.

3. Consider the chemical pathway shown in fig 4 above.

a. Give the IUPAC name for lactic acid. ________*2-hydroxypropanoic acid*_______________ ***1 mark***

b. Identify the following: reagent:

Reagent Y _____________*H_2O/ H_3PO_4(s)/ 300°C*___________________ ***1 mark***
Reagent X ______________ *$Cr_2O_7^{2-}$/H^+(aq)*____________________ ***1 mark***
Substance W ____________ *ethanol* ***1 mark***
Substance Z _____________*ethanal*________________________ ***1 mark***

c. A student was asked to identify the type of reaction that converts lactonitrile to lactic acid? Their response was that the reaction is a *"hydration reaction"*

i. Is the student correct? __________*No*________________________________ ***1 mark***

ii. Justify your response to i. above.

Hydration involves the addition of H_2O across a carbon-to-carbon double bond. Hydrolysis involves the breaking of covalent bonds to create, by the addition of H_2O, two new molecules. *-------- 1 mark*

$CH_3CH(OH)CN + 2H_2O \rightarrow CH_3CH(OH)COOH + NH_3$ *----- 1 mark*

d. Consider the reaction pathway shown below.

i. In the box provided give the names of T, S and W. ***3 marks***

T = methanol S = H_2SO_4(l) W = H_2O

lactic acid + [T] —[S]→ methyl lactate + [W]

ii. Give the specific name for this type of reaction. ___*esterification*________________ ***1 mark***

e. Consider the information shown in table 1.

i. With reference to specific functional groups and intermolecular bonding, explain why methyl lactate has a lower boiling temperature than lactic acid even though it is a bigger molecule.

Substance	BP at 1 atm (°C)
Lactic acid	217
Methyl lactate	145

Table 1- boiling temperatures of lactic acid and methyl lactate at 1 atm.

Lactic acid has a carboxyl group and a hydroxyl functional group whilst methyl lactate has dipole-dipole. Both molecules also have dispersion forces. *------- 1 mark*

Hydrogen bonding provides a stronger intermolecular force of attraction than dipole-dipole. Dispersion forces are inconsequential when compared with strong h-bonds and dipole-dipole, especially when the relative molecular sies do not differ significantly. *------ 1 mark*

Stronger forces of attraction in intermolecular forces of attraction require a greater energy to break. Hence a higher BP. *----- 1 mark*

f. When purifying lactic acid from the reaction mixture distillation is used. Using your knowledge of chemistry and the information given to you in the extract above. Suggest a reason why the formation of methyl lactate is necessary.

Distillation requires the compound be increased to its BP. Lactic acid has a BP of approximately 216 °C at which point it would decompose and significantly reduce the yield *----------- 1 mark*

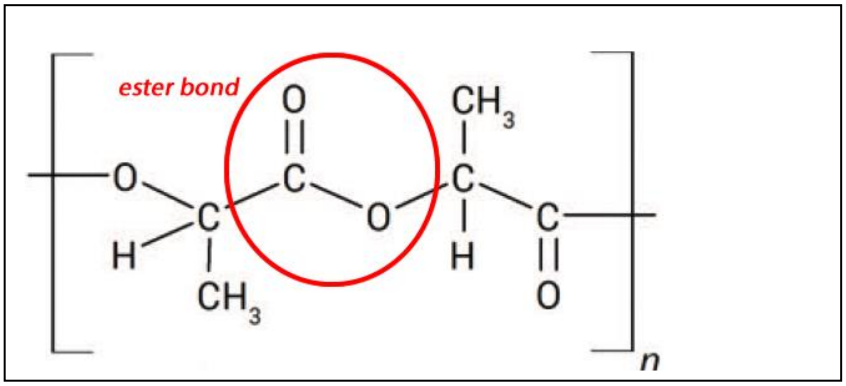
Methyl lactate on the other hand has a BP of 145 at atmospheric pressure and is able to withstand the separating technique of fractional distillation with decomposition. *--------- 1 mark*

g. In the box below:

i. draw a small, two monomer, section of the polylactic acid. ***2 marks***

correct structure -------- 1 mark

every bond shown ------ 1 mark



ii. In the box above, circle and clearly label a functional group present in your diagram of the small section of polylactic acid ***2 marks***

-------- 1 mark for ester

-------- 1 mark for correct identification.

iii. Calculate the atom economy for the reaction of five lactic acid (formula mass = 90.09 amu) monomers to form a small section of PLA. Give your answer to the right number of significant figures. ***3 marks***

% atom economy = (mass of desired product / total mass of reactants) X 100 ---- 1 mark

=> (450.45 – 4 X 18.0)/(5 X 90.09) = (378.45 /450.45) X 100 = 84.0 % ----- 1 mark

sig figs ----- 1 mark

4. Does the use of PLA as a plastic material made from ethene derived from the petrochemical industry represent a circular or linear economy? Define the terms "linear economy" and "circular economy," and explain your reasoning.

Linear Economy: follows a "take-make-dispose" model. Resources are extracted, transformed into products, and eventually discarded as waste after use. Or any other clear and accurate definition
----- 1 mark

Circular Economy: follows a "make-use-recycle" or "take-make-reuse" model, where products and materials are kept in use for as long as possible through recycling, reusing, refurbishing, and remanufacturing. Or any other clear and accurate definition. *----- 1 mark*

The chemical synthesis of lactic acid from ethene as a feedstock is an example of a linear economy.
------ 1mark
The use of ethene derived from the petrochemical industry to produce PLA represents a linear economy. This is because it relies on non-renewable resources and follows a take-make-dispose model at least in the initial stages.
----- 1 mark

5. Which two sustainable development goals are addressed by the use of fermentation to produce lactic acid for the synthesis of PLA? Justify your selection of each goal.

Goal 12: Responsible Consumption and Production ***--------- 1 mark***

- ***Justification***: *---------1 mark for a valid justification*
  - ***Sustainable Production***: *Fermentation to produce lactic acid uses renewable resources like corn starch or sugarcane instead of non-renewable petroleum-based resources. This promotes sustainable production practices.*
  - ***Reduction of Waste***: *PLA is biodegradable, which helps reduce plastic waste in the environment. By using biodegradable plastics, we minimize the impact of plastic pollution, aligning with the goal of reducing waste generation through prevention, reduction, recycling, and reuse*

Goal 13: Climate Action ***------- 1 mark***

- ***Justification***: *------ 1 mark for a valid justification*
  - ***Lower Carbon Footprint***: *The production of lactic acid via fermentation generally has a lower carbon footprint compared to traditional petrochemical processes used to produce plastics. This reduction in greenhouse gas emissions helps combat climate change.*
  - ***Renewable Resources***: *Utilizing renewable resources for PLA production helps decrease reliance on fossil fuels, further reducing the carbon footprint associated with plastic production and disposal.*

Other valid suggestions accepted.

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