Effect of Temperature on Chemical Recycling of Polylactic Acid

Investigating the effect of varying temperatures (40, 60, 70 and 80 °C) on the hydrolysis of polylactic acid in a 50% ethanol solution by measuring lactic acid production

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Introduction

The global production of plastics has seen a significant increase over the years. In 2019, the production was approximately 368 billion tons, and it is expected to further increase to about 600 billion tons in 2025. More than half of the 9.2 billion tons of plastic produced up to now, around 5 billion tons have ended up as waste, with between 5 and 13 million tons entering the oceans (*Plastic Soup Foundation*). Unfortunately, these polymers have extremely long degradation lifetimes, lasting anywhere from 500 to 1000 years without breaking down (*Lubofsky*). Despite efforts to accelerate degradation using composting enzymes and bacteria, the process remains slow.

The persistence of plastics in landfills for such extended periods is a cause for concern. Moreover, the traditional production of plastics relies on nonrenewable petroleum resources. Considering the complete lifecycle of plastics is essential when exploring alternative options, as their integration into society is widespread. This has prompted chemists to actively investigate new manufacturing practices.

One promising alternative is polylactic acid (PLA), a biodegradable polymer derived from natural resources. PLA is created using lactic acid, which is derived from corn, as the monomer. Under industrial compost conditions, PLA degrades into harmless components such as CO_2, H_2O, and humus. It typically breaks down within approximately 180 days. The biodegradability of PLA significantly reduces the volume of waste sent to landfills.

The polymer is made from corn feedstock, so it uses significantly less petroleum than traditional polymers. While PLA is recyclable, no municipal recycling facilities accept it at this time. At the end of the product's useful life, PLA products can also be reused as other products instead of being disposed of in landfills or compost facilities. Chemical recycling converts PLA back to its monomer Lactic Acid by hydrolysis, so it can then be used as raw material for new PLA production (Figure 1).

Figure 1. End of life management processes for PLA | *Bioplastics News*

Background Information

Hydrolysis, derived from the Greek words "hydro" meaning water and "lysis" meaning to split, is the process through which polymers are broken down into their constituent monomers with the help of water molecules. (*LibreTexts*). In this context the added water in the ethanol solution hydrolyses the bonds in the compound and causes breakdown.
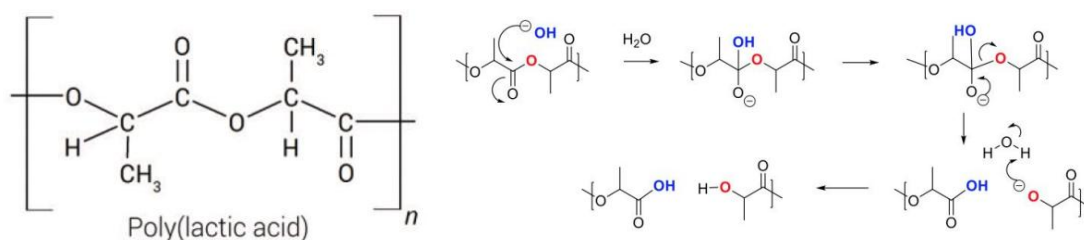

Figure 2. In basic conditions, PLA hydrolyzes as follows: A hydroxide ion from the solution attaches to the carbonyl carbon atom. This leads to electron transfer, breaking the bond between the carbon atom and the oxygen atom. Subsequently, the oxygen atom forms a bond with a hydrogen atom from a water molecule. This process repeats until the PLA polymer chain disintegrates into lactic acid, its monomer. | *Hydrolysis of Post-Consumer Polylactic Acid Waste by Rich Gurney at Simmons College*

Temperature plays a significant role in chemical reactions, often affecting reaction rates and product yields. In the context of PLA hydrolysis, higher temperatures are generally associated with increased reaction rates. This is because elevated temperatures provide more thermal energy, facilitating the disruption of chemical bonds in the polymer chains and accelerating the hydrolysis process.

Understanding the relationship between temperature and PLA hydrolysis is crucial for developing efficient degradation methods and eco-friendly materials. By systematically investigating how varying temperatures (40, 60, 70, and 80 °C) influence the hydrolysis of PLA in a 50% ethanol solutions, the aim is to elucidate the optimal temperature conditions for maximizing lactic acid production.

Hydrolytic degradation of PLA in water-ethanol solutions occurs more rapidly when PLA is exposed to a 50% water-ethanol mixture compared to other concentrations (Iñiguez-Franco, Auras). Ethanol molecules allow faster water penetration into the PLA matrix due to initiation of chain cleavage. Temperatures higher than the melting temperature of PLA can lead to degradation of Lactic Acid. Thus a range of lower and medium temperatures ranging from 40-80 °C is preferred (PlastikCity).

Colorimetry is a technique used to determine the concentration of colored substances in solutions by measuring the amount of light absorbed at a specific wavelength. The wavelength of light used is crucial and must match the wavelength absorbed by the substance being analyzed.
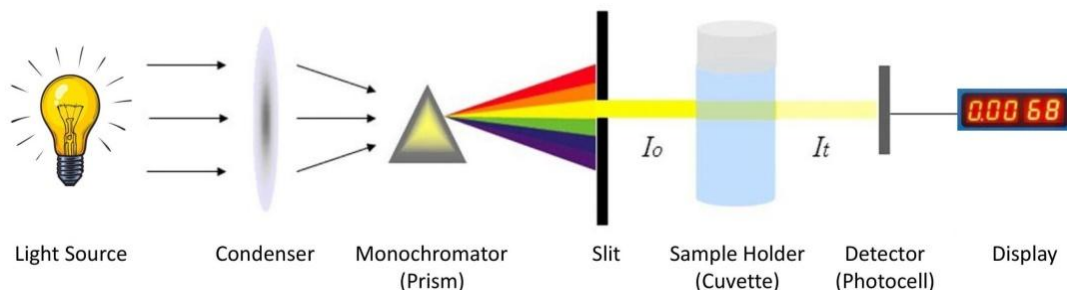
Figure 3. Instrumentation of colorimeter | laboratorytests.org

In this study, a reddish-orange complex is formed so a wavelength of around 450-500 nm is used.

$$FeCl_3 + C_3H_6O_3 \rightarrow [Fe(C_3H_5O_3)_3] + 3HCl$$

The Beer-Lambert law forms the foundation of colorimetry, establishing that the absorbance of a solution is directly proportional to both its concentration and the path length of the solution. The law is expressed by the equation:

Where A is the absorbance of the solution,

ε is the molar absorptivity (also called the molar extinction coefficient), which is a constant specific to the solute and the wavelength of light used that can be determined by plotting a graph relating absorbance to known concentrations of the solute,

c is the concentration of the solute in the solution,

and b is the path length of the light through the solution.

Research question

Thus, to understand optimal conditions for industrial processes for PLA degradation, the most efficient temperature conditions for hydrolysis must be explored. Keeping this in mind, the following research question is formulated with the goal of developing eco-friendly materials and processes to reduce the environmental impact of plastic waste, and gaining more knowledge tin the fundamentals of polymer chemistry.

How do varying temperatures (40, 60, 70 and 80 °C) affect the hydrolysis of Polylactic acid in 50% ethanol solution in terms of concentration of lactic acid produced?

Hypothesis

Given the general understanding that higher temperatures often lead to increased reaction rates, it is anticipated that the hydrolysis of Polylactic acid (PLA) in a 50% ethanol solution will follow this trend. Specifically, it is hypothesized that the temperature of 80 °C will likely result in the highest concentration of lactic acid produced. The assumption is that higher temperatures will accelerate the hydrolysis process, allowing for more efficient breakdown of PLA into lactic acid molecules.

Preliminary Trials

In the preliminary trials, hydrolysis was observed in solutions of 100% ethanol, 50% ethanol and 0% ethanol. A span of 30 minutes was observed for each of these, to discover that there was little to no change in the PLA pieces physically. While 50% ethanol solution yielded the best results, there was still very minimal change in 30 mins, suggesting that the some significant change to be observed will take a much longer time. Thus to catalyze this process, as studied in a chapter of ACS Chemistry, the addition of NaOH ensures proper breakdown of PLA acting as a substitute for microorganisms in the environment, as it aids in surface modification of PLA. Conducting the experiment with an ethanol-NaOH solution was concluded to be most suitable as it provided the necessary results within 20 minutes.

Variables

Table 1. Independent and Dependent Variables

Variable type	Variable	Significance
Independent Variable	Temperature	To see the effect of temperature on hydrolysis of PLA, a temperature range of 40, 60, 70 and 80 °C is compared to concentrations of lactic acid produced.
Dependent Variable	Absorbance (Concentration of lactic acid produced)	The absorbance of the iron (iii) lactate complex is tested by the colorimeter and is correlated to concentration of lactic acid during data processing. 5 trials are conducted for the 4 different temperatures to minimize uncertainty.

Table 2. Control Variables

Variable	Method of control	Significance
PLA weight	The weight of PLA is carefully measured and maintained at 2.0 grams for each trial.	If the weight of PLA is not controlled, an additional unaccounted for independent variable is introduced, leading to unreliable results.
Solution for Hydrolysis	2 g of PLA is placed in a 50% ethanol-NaOH solution of 40 ml.	Inconsistent concentrations can lead to variable reaction rates, making it difficult to isolate and analyze the impact of temperature on the hydrolysis rate.
Reaction time	The PLA is hydrolyzed for a period of 20 minutes and stirred at a constant RPM.	Allows for a fair and accurate comparison of temperatures on the hydrolytic degradation.
Concentration of HCl	6M HCl is added until pH is around 4.	To neutralize solution and maintain consistent concentrations to prevent addition of unaccounted variables.
Concentration and amount of Ferric chloride reagent	To check for absorbance, 2 drops of 0.1M of Ferric chloride is added.	Inconsistencies in the amount of ferric chloride added can lead to variations in color development.
Wavelength in colorimeter	Wavelength set to 500 nm on colorimeter.	The absorbance of a sample is wavelength-dependent. If the wavelength setting on the colorimeter is not consistent between trials, it can result in inaccurate absorbance measurements.

Apparatus

Table 3. Apparatus and uncertainties

Equipment	Uncertainty
Volumetric flask (100 ml)	± 0.08 ml
Beaker	± 0.1mL
Measuring cylinder	± 0.5mL
Hot plate stirrer	± 0.5°C
Thermometer	± 0.5°C
Weighing balance	± 0.001g
Pipette	± 0.02 mL
Colorimeter, cuvettes	± 0.001

Table 4. Solutions prepared

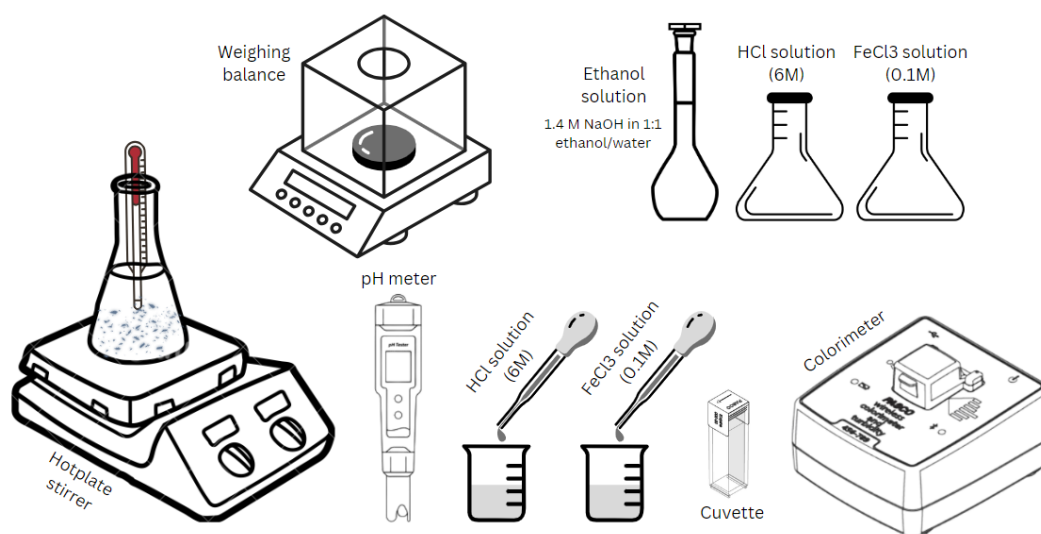| Solution	Amount	Concentration
Ethanol solution	40 ml (x20)	1.4 M NaOH in 1:1 ethanol/water
HCl	0.5 ml (x20)	6M
Ferric Chloride	0.1 ml (x20)	0.1M

Figure 4. Sketch of experimental set-up

Safety, Ethical and Environmental Considerations

1. Appropriate precautionary equipment, including lab coats, gloves, and safety goggles, was worn to protect against potential chemical splashes or contact with heated substances.
2. Ethanol Handling: Ethanol, being flammable, was used cautiously, and the experiment was performed away from heat sources. Ethanol solutions were stored safely.
3. Heating Precautions: The hot plate was handled with care to prevent burns, and appropriate tools, such as tongs or heat-resistant gloves, were used when manipulating hot materials.
4. Colorimeter Usage: The colorimeter was handled with care to avoid damage. Manufacturer guidelines for calibration and maintenance were followed, and it was used according to the instrument's specifications.
5. Waste Disposal: Waste materials, including PLA residues and used solutions, were disposed of according to local regulations and laboratory waste disposal guidelines. Ethanol waste was managed in compliance with specific disposal requirements.
6. Direct contact with Iron (III) chloride was avoided, though it only had a small concentration, as it can potentially cause irritation to the eyes.

Methodology

1. Firstly, PLA pieces are cut into similar-sized pieces. The smaller the pieces, the faster the reaction.
2. 40 ml of ethanol-NaOH solution is prepared, where 20 mL of 50% ethanol-water solution is added to 20 mL of NaOH in a beaker after being measured with the help of a measuring cylinder.
3. This solution is brought to the desired temperature on the hotplate stirrer for a few minutes before 2 g of PLA pieces are measured on a weighing balance and added to the beaker. The desired temperature is confirmed with the help of a thermometer.
4. The solution is left to be stirred for a period of 20 minutes at the desired temperature, after which it is left to cool.
5. To neutralize the solution, around 0.5 ml of 6M HCl is added to the solution. To make sure the solution is alkaline; a pH meter is used to confirm pH of the solution to be around 4.
6. Then, to check the amount of lactic acid that has been evolved from hydrolysis, around 0.1ml of a reagent such as ferric chloride at 0.1M is added with the help of a dropper.
7. Finally, the colorimeter is set up at 500 nm. After calibration, the solution containing the iron (iii) lactate complex formed is added to a cuvette. The cuvette is placed in the colorimeter to record an absorbance value.
8. These steps are repeated for 5 trials at each of the 4 temperatures (40, 60, 70 and 80 °C).

Data Collection

Table 5. Calibration Data

Iron(III) Lactate (moles litre^{-1})	Absorbance at 500 nm (± 0.001)
-	0.000
1.0	0.022
2.0	0.040
3.0	0.060
4.0	0.078
5.0	0.102
6.0	0.120
7.0	0.140
8.0	0.160

Table 6. Absorbance of Iron (III) Lactate Complex at 500 nm as determined by colorimeter

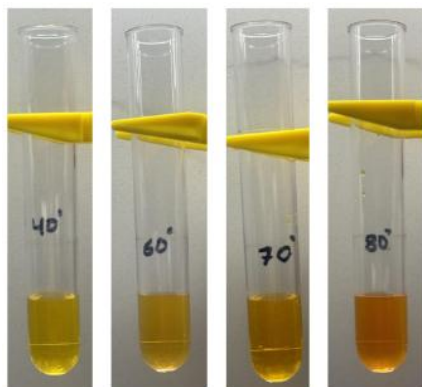| Temperature ($\pm 0.5°C$)	(Absorbance Value) (± 0.001)				
	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
40°C	0.81	0.93	0.96	0.87	0.84
60°C	0.99	0.89	0.8	0.92	0.88
70°C	0.98	0.93	1.1	1.02	0.97
80°C	1.05	1.2	0.99	1.15	1.1

Figure 1. A yellowish orange to reddish orange was observed when the ferric chloride was added to the solution.
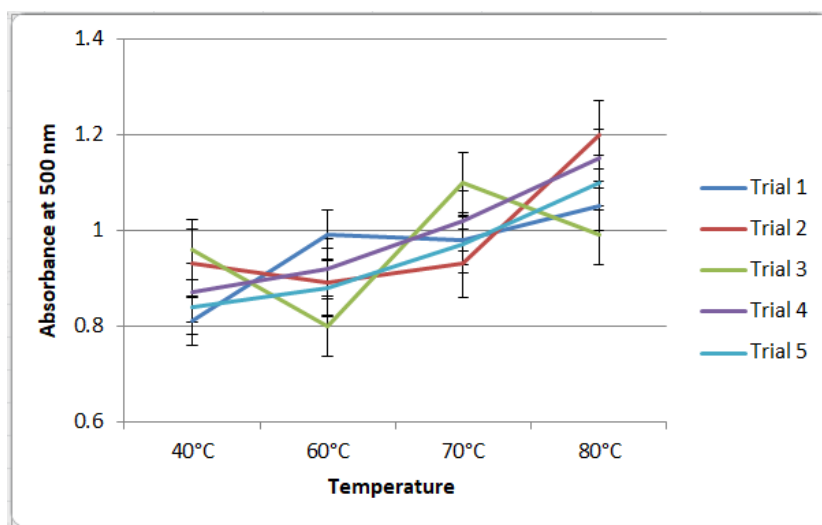
Data Processing

Figure 6. Temperature vs Absorbance

$$A = \varepsilon bc, \text{ where}$$

A = values in table,

ε = molar absorptivity to be calculated as per calibration data collected,

c = concentration of the solute in the solution to be calculated,

b = 10 mm,

To calculate ε,

We know that there is a linear relationship between absorbance and concentration.

So, linear regression is plotted with the help of the calibration data, using the software Desmos.
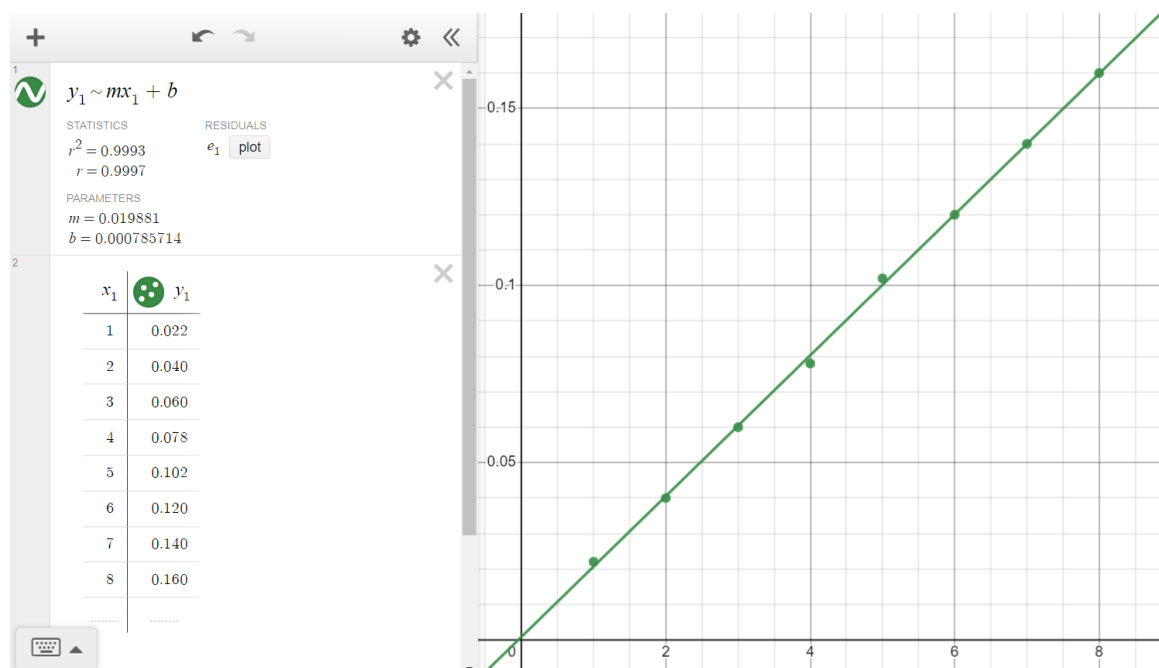

Figure 7. Linear Regression obtained on Desmos by inputting calibration data

$$A = 0.01988c + 0.0007$$

Now with the experimentally collected absorbance values, the concentration can be calculated to plot on a concentration vs temperature graph.

Table 7. Concentration of Iron (III) Lactate Complex formed as calculated:

	Concentration $= \dfrac{A - 0.0007}{0.01988}$ (mol dm-3)				
Temperature	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
40°C	40.68	46.80	48.77	43.75	42.14
60°C	49.61	44.65	39.54	46.33	44.16
70°C	49.27	46.80	55.88	51.25	48.88
80°C	52.73	60.39	49.81	57.75	55.38

$$FeCl3 + C3H6O3 \rightarrow [Fe(C3H5O3)3] + 3HCl$$
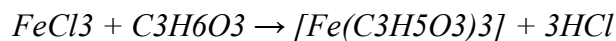
From this reaction, we see that one mole of ferric chloride reacts with one mole of lactic acid to form one mole of the complex [Fe(C3H5O3)3]. Therefore, the stoichiometry is 1:1 between ferric chloride and lactic acid.

Since the stoichiometric coefficients for both lactic acid (C3H6O3) and the product [Fe(C3H5O3)3] are 1 in the balanced equation, the concentration of lactic acid (C3H6O3) can be assumed to be the same as the concentration of the product [Fe(C3H5O3)3].

It is important to note that this is done under the assumption that all the lactic acid reacts with the ferric chloride solution to produce the iron lactate complex, and are hence in the same exact ratio.

Table 8. Concentration of Lactic acid formed as calculated

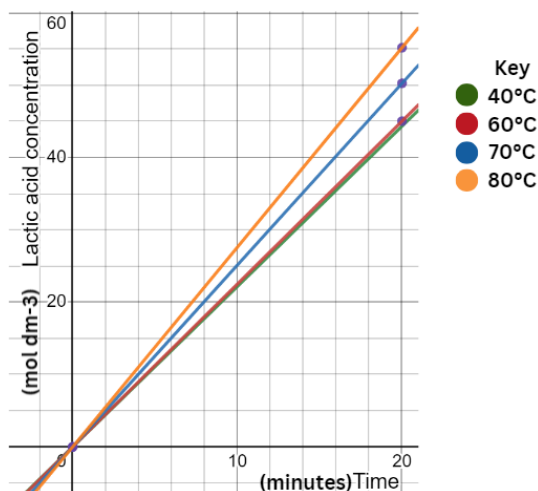| Temperature	Concentration of Lactic Acid (mol dm^{-3}) after 20 mins				
	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
40°C	40.68	46.80	48.77	43.75	42.14
60°C	49.61	44.65	39.54	46.33	44.16
70°C	49.27	46.80	55.88	51.25	48.88
80°C	52.73	60.39	49.81	57.75	55.38

Figure 8. Lactic acid concentration vs Time for temperatures 40, 60, 70 and 80°C

Uncertainty Propagation

To obtain precise values after processing the data, it is important to calculate the percentage and absolute certainties. The following steps are undertaken to do so:

1. Mean Absorbance: The average of the absorbance values from each of the five trials is calculated for each temperature, as it provides a central tendency measure.
2. The mean absorbance value obtained in step 1 is used to calculate the concentration of lactic acid produced using the provided formula as obtained from the linear regression:

$$\text{Concentration} = \frac{\text{Mean Absorbance} - 0.0007}{0.01988}$$

3. The absolute uncertainty was calculated using the absorbance values from each trial at the specific temperature. The standard deviation of these absorbance values was calculated to find the uncertainty associated with the mean absorbance. The calculation of the deviations of each individual absorbance value from the mean absorbance was squared and their sum was calculated, and then the square root of the variance was taken to obtain the standard deviation.
4. The absolute uncertainty as a percentage of the mean absorbance was calculated to obtain the percentage uncertainty. This was done by dividing the absolute uncertainty by the mean absorbance and multiplying by 100.

For example, for a trial with temperature 40°C

1) $\text{Mean Absorbance} = \frac{0.81 + 0.93 + 0.96 + 0.87 + 0.84}{5} = 0.882$

2) $\text{Concentration} = \frac{0.882 - 0.0007}{0.01988} = \frac{0.8813}{0.01988} = 44.23 \text{ mol dm}^{-3}$

3) $\text{Deviations from mean} = (0.81 - 0.882) = -0.072, (0.93 - 0.882) = 0.048, (0.96 - 0.882) = 0.078, (0.87 - 0.882) = -0.012, (0.84 - 0.882) = -0.042$

4) $\text{Sum of squares of deviations} = (-0.072)^2 + (0.048)^2 + (0.078)^2 + (-0.012)^2 + (-0.042)^2 = 0.01444 + 0.002304 + 0.006084 + 0.000144 + 0.001764 = 0.024736$

5) $\text{Variance} = \frac{0.024736}{5-1} = 0.006184$

6) $\text{Standard Deviation} = \sqrt{0.006184} = 0.07868$

7) $\text{Absolute Uncertainty} = 0.07868$

8) $\text{Percentage Uncertainty} = \frac{0.07868}{0.882} \times 100 = 8.92\%$

Table 9. Uncertainty Propagation as calculated for each temperature

Temperature (°C)	Mean Absorbance	Concentration (mol dm^-3)	Absolute Uncertainty	Percentage Uncertainty (%)
40	0.882	44.23	0.07868	8.92
60	0.896	45.00	0.06876	7.67
70	1.00	50.23	0.06443	6.44
80	1.098	55.25	0.08076	7.36

Analysis

Upon analysis of the data, it is evident that there is a clear trend of increasing absorbance values with increasing temperature. At 40°C, the average absorbance value is 0.882, which then increases to 0.896 at 60°C, 1.000 at 70°C, and 1.098 at 80°C. This trend suggests that higher temperatures promote a more rapid hydrolysis of PLA, resulting in higher concentrations of lactic acid being produced within the given timeframe of 20 minutes.

The percentage uncertainty values range from approximately 6.44% to 8.92% across the different temperatures. A higher percentage uncertainty suggests greater variability or imprecision in the absorbance measurements. In this context, percentage uncertainties around 8-9% are relatively moderate but not negligible.

Systematic errors could arise from factors such as instrumental limitations, calibration issues, or procedural biases. These errors may contribute to the overall uncertainty by introducing consistent deviations in the measurements. While the percentage uncertainties are not exceptionally high, they still represent a significant level of variability in the measurements. This variability could potentially affect the accuracy and reliability of the conclusions drawn from the data.

Conclusion

The conducted investigation thus helps come to a conclusion based on the research question proposed at the beginning of the work: How do varying temperatures ((40, 60, 70 and 80 °C) affect the hydrolysis of Polylactic acid in 50% ethanol solution in terms of concentration of lactic acid produced? The trend indicating a strong positive linear relationship between temperature and lactic acid produced, as mentioned in the analysis is consistent with the principles of chemical kinetics, where higher temperatures often lead to increased reaction rates. In the context of PLA hydrolysis, higher temperatures likely accelerate the breakdown of PLA polymer chains into lactic acid monomers. Thus, referring back to our hypothesis, it can be confirmed that the temperature of 80°C produced the highest concentration of lactic acid.

In the hydrolytic degradation process of PLA, the number of carboxylic acid chain ends increases, leading to a self-catalyzed reaction. This occurs due to the buildup of acidic polymer fragments within the specimens, facilitating the hydrolysis process. As seen in Figure.5, a positive linear relationship between time and concentration of lactic acid is observed at different temperatures. In reality, the relationship between PLA degradation and time should exhibit an exponential trend, with degradation decreasing over time until it reaches a plateau. However, due to the limited exposure time of only 20 minutes, there wasn't a significant amount of PLA degradation observed. The analysis was also impacted by systematic errors, which became apparent later in the exploration process. It was only then that methods to improve the accuracy of the results were realized.

On observing Figure 5, it can be noticed that the slope of the graph between 40°C and 60°C is very close, suggesting that a relatively similar rate of increase in lactic acid concentration within this temperature range. Moving to higher temperatures, the concentration of lactic acid increases. At 70°C, there's a considerable jump in concentration compared to 60°C, indicating a faster rate of hydrolysis at this temperature. At 80°C, the concentration of lactic acid reaches its peak, indicating the highest rate of PLA degradation among the temperatures tested.

Evaluation of Errors

Table 10. Systematic and Random Errors as determined

Areas of improvement	Significance of error	Improvement
At all temperatures, it was observed that there remained some undissolved PLA in the solution. (Systematic Error)	This error compromises the reliability and validity as it can lead to inaccurate measurements.	To ensure all PLA dissolves, a stronger concentration of NaOH can be added to the solution.
The solutions were left on the stirrer for a relatively brief period. (Systematic Error)	Due to time constraints, the absorbance for each temperature was only recorded for 20 minutes, resulting in limited hydrolysis of PLA during this timeframe. Thus, the full impact of temperature on PLA hydrolysis and the precise concentration of lactic acid produced cannot be accurately determined.	Due to time constraints during the experiment, conducting trials longer than 20 minutes was impractical. Longer trials, spanning 3-4 hours, would provide better results, with more defined graphs of the exponential pattern to be observed.
Fluctuation in absorbance readings from the PASCO Colorimeter on SparkVue (Random Error)	The fluctuation observed in the colorimeter readings, with values changing randomly, likely contributed to random errors in the experiment.	A more precise colorimeter would enhance the accuracy of absorbance readings by minimizing stray light and ensuring that all UV light is directed solely at the sample, thereby reducing potential sources of error in the experiment.

Further Extension to the Experiment

       Exploring temperature as a variable was insightful, but for future experiments, a similar approach could be taken to precisely determine the rate of PLA hydrolysis at various temperatures. The data collection process would remain consistent, with temperature as the independent variable and absorbance as the dependent variable. Readings would be taken at more specific time intervals and utilizing logarithms, an Arrhenius plot could be constructed to ascertain the activation energy required for PLA decomposition. Additionally, the Arrhenius plot's slope could be used to determine the rate constant for the reaction at room temperature. Beyond temperature, other factors also influence PLA hydrolysis rates. Instead of temperature, the independent variable could be the pH of the solution, exploring its impact on PLA degradation rates.

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