CHALMERS

Synthesis of lactide using residual product from Kraft process

Lab-scale process and upscale cost estimation

Bachelor of Science thesis in Chemical Engineering

Bryan Strömberg
Nuuro Josoph

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING

CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2021
www.chalmers.se

Synthesis of lactide using residual product from Kraft process
Lab-scale process and upscale cost estimation
BRYAN L. STRÖMBERG & NUURO JOSOPH

Supervisor: PhD Amit, Chemistry and Chemical Engineering, Organic Chemistry.
Examiner: Prof. Gunnar Westman, Chemistry and Chemical Engineering, Organic Chemistry.

Department of Chemistry and Chemical Engineering or Technology
Chalmers University of Technology
SE-412 96 Gothenburg
Sweden
Telephone + 46 (0)31-772 1000

Acknowledgements

Our most sincere gratitude goes to our supervisor and examiner **Prof. Gunnar Westman** for his incredible patience for answering all of our never-ending questions, his guidance, expertise and feedback throughout our work.

We would also like to give a special thanks to our beloved families and friends. We could not have completed this task without their support.

Bryan Strömberg, June 2021.
Nuuro Josoph, June 2021.

ABSTRACT

Polylactic acid (PLA) has received a great amount of interest as an alternative polymer to the conventional fossil-based polymers, considering PLA derives from plant-based raw materials, such as sugar cane, sugar beet and cellulose. PLA is most commonly produced using two different processes, either direct polycondensation, or by ring-opening polymerization (*ROP*). Synthesis of lactide via ROP using the residual stream from pulp production, as well as an additional method of utilizing microwave irradiation, gets examined.

The main goal of this thesis was the synthesis of lactide using a residual product from the pulp industry, which had a lactic acid content estimated at ~10%. ^{1}H NMR spectrums were utilized to determine the formation and molecular weight of ethyl lactate, lactide and PLA.

Crude lactic acid (LA_w) was successfully purified with activated charcoal. The esterification of lactic acid showcased excellent conversion to ethyl lactate with a maximum 20% water content. The synthesis of ethyl lactate using LA_w was similarly successful however with low yield and purity. The catalyst used was stannous octoate ($Sn(Oct)_2$) with a reaction temperature of 80°C. Lactide was also synthesized in two attempts, with zinc oxide proving to be the most effective at 220°C. Synthesis of PLA was possible using microwave irradiation in 30 min with 180°C being the optimal temperature, however in small amounts.

In conclusion, synthesis of ethyl lactate from crude lactic acid was successful, while following reactions resulted in poor yields. Lactide was synthesized using pure lactic acid as starting material, rather than the impure LA_W. A plausible cause of the low yields were the lack of low pressure in the lactide synthesis and inert conditions in the microwave reactions.

Keywords: PLA, polylactic acid, lactic acid, lactide, pulp, ROP, stannous octoate, zinc oxide, purification, ethyl lactate

LIST OF ABBREVIATIONS

PLA	Polylactic acid, polylactide
LA	Lactic acid
LA_W	Residual product from pulp industry, containing water, crude lactic acid ~10% and unknown impurities.
LA_{W20}	LA_W, concentrated to ~20%
(G)AC	(Granular) Activated carbon
$Sn(Oct)_2$	Stannous octoate, Tin(II) 2-ethylhexanoate
p-TsOH	*para*-Toluenesulfonic acid
EtLA	Ethyl lactate
ROP	Ring-opening Polymerization
ZnO	Zinc oxide

TABLE OF CONTENTS

1. Introduction

This thesis is done through Chalmers Industriteknik and they are a part of a project conducted by RISE Proccesum, collaborating alongside Domsjö factories, Add North and Sustainable Chemicals Future.

1.1 Polylactic acid

Polylactic acid (PLA) is a relatively new sort of biodegradable plastic constructed from lactic acid. The lactic acid is produced either via chemical synthesis or bacterial fermentation. PLA has received a great deal of interest as an alternative polymer to the conventional fossil-based polymers, since lactic acid can be derived from plant-based raw materials, such as sugar cane, sugar beet and corn (starch). Another suitable and promising source of lactic acid is pulp, which contains hemi- and lignocellulose and has been shown to be able to enzymatically convert into glucose. In this process, glucose would be converted into lactic acid. Lactide is the dimer form of lactic acid and opening the molecule via ring-opening polymerization (ROP) is the most commonly used method to manufacture PLA (John, R. P. et al., 2007).

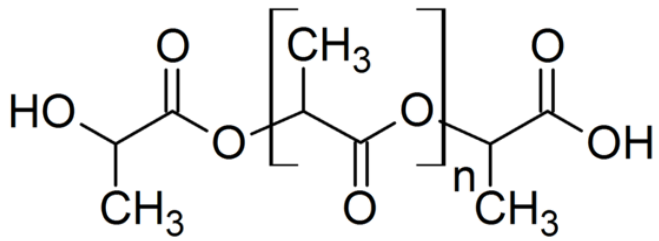


Figure 1. The chemical structure of polylactic acid.

1.2 The use of residual products from pulp production

The most currently used process for the production of pulp is the Kraft process, which uses sodium hydroxide and sodium sulfate to produce wood pulp. This method of producing pulp accounts for 70% of the global pulp production (Möllersten et al., 2019). Wood is mainly composed of cellulose fibers, lignin and hemicellulose. The wood gets cooked in pulping chemicals, sodium hydroxide (NaOH) and sodium sulfate (Na_2SO_4) (Tran, H. & Vakkilainnen, E., 2016). Paper sludge is a residual product of the Kraft process and this seemingly unwanted by-product, is now a promising, new raw material, since it does not have to be pretreated before use, unlike cellulose. The sludge has already gone through a process of delignification using cooking chemicals and steam while in the pulp production (Takano, M., & Hoshino, K., 2016). The paper sludge contains residues of lignin, hemicellulose, organic binders, inorganic compounds such as paper additives and traces of heavy metals (Kuokkanen, T. et al., 2008).

Due to its high content of polysaccharides, the paper sludge can be enzymatically hydrolyzed into monomers (for example lactic acid). The method of enzymatic hydrolysis, as opposed to acid hydrolysis, is favored due to the reaction conditions being relatively mild and the avoidance of using toxic and corrosive chemicals (Marques, S. et al., 2008). The process of hydrolysis of cellulose can get inhibited by the paper additives (inorganic compounds), since the pH of the reaction is, to some extent, quite higher than what would be optimal for the enzymatic conversion (Kang, L et al. 2010). Considering that wood is one of Sweden's most abundant natural resources, and the sixth largest producer and third largest exporter in the world (''Trä och träindustrin'', n.d.), a production of PLA

derived from the residual products of the forest- and paper industry, has the possibility of becoming a great export for Sweden.

1.3 Purpose and scope

The main goal of RISE Processum's project is to find a method of producing PLA by using the lactic acid byproduct from the Kraft process. This thesis' goal is to produce 5 grams of lactide from a provided lactic acid solution, LA_W, given by RISE Processum, which in addition to large amounts of water, also contains indeterminate organic and inorganic impurities.

Two different methods of synthesis will be used, microwave irradiation and distillation with different choice of catalysts, temperatures and reaction times. In addition, a quantification and estimation of the cost of the materials utilized in the process is examined.

Parameters that are investigated:

- How does the amount of water in the sample affect the yield?
- How to separate the impurities from enzymatically treated cellulose?
- Which methods are effective for production of lactide?

Literature and data search, molecular characterization with the use of ^{1}H NMR, software for design and evaluation of experimental results and training in report writing and presentation techniques, will be used to find significant results. Some limitations are present during the work of this thesis, as the COVID-19 pandemic has led to multiple restrictions within the Chalmers University of Technology and their facilities. The most significant limitation is the precautions of meeting and researching together as a group. In addition, many resources could not be accommodated if the materials or machinery were not available.

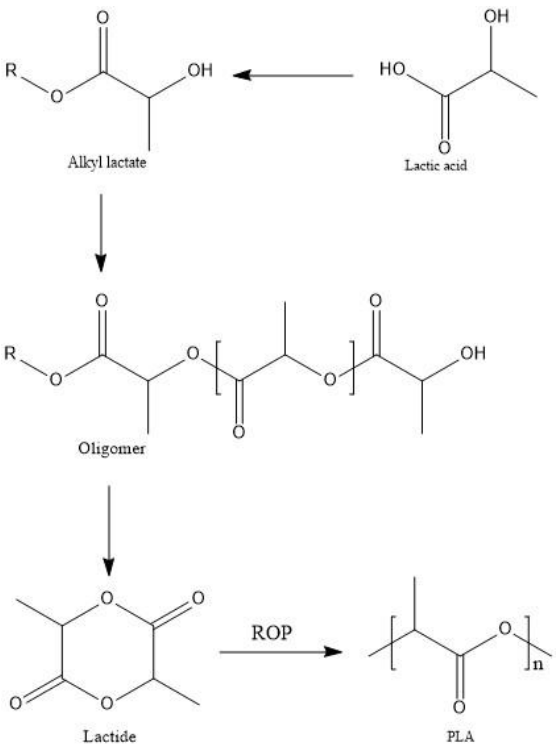
2. Theory

2.1 Purification and recovery of lactic acid and alkyl esters

Recovery of lactic acid from fermentation broth using granular activated carbon (GAC) has been proposed as a suitable and green method (Gao, M., et al. 2011). GAC is a porous form of carbon derived mainly from carbonaceous materials, such as woody, cellulose plants. Its porosity contributes to a high surface area, which is ideal for adsorption (Water Treatment Solutions. n.d.). The granular form of activated carbon can be reactivated by undergoing regeneration with the intention of removing the adsorbed components on the surface, thereby making GAC a promising material, both from an economical and environmental point of view (Ebben, A., Carlson, C.. 2021). The most commonly used methods of regeneration are steam regeneration, solvent regeneration, chemical regeneration and thermal regeneration (Cooney, D.O. et al. 1983; Guo, D. et al. 2011; Sun, K. et al. 2009; Guo, Y., & Du, E., 2012). Microwave-assisted regeneration of AC has been shown to be a relatively new and promising method, however additional studies need to be performed (Foo, K., & Hameed, B. 2012)

Acetone has been shown to desorb lactic acid from the surface of AC while also acting as a cleaner by avoiding fouling onto GAC. The optical purity of the lactic acid does not decrease using acetone, reaching 99.5% optical purity. Acetone has the possibility of being recovered via evaporation and utilized multiple times, making the process more efficient and resourceful (Gao, M., et al. 2011).

An additional recovery method involves synthesizing an alkyl lactate in the fermentation broth of lactic acid production, with the purpose of achieving either pure lactic acid or alternatively an oligomer of ethyl lactate. The esterification of the crude lactic acid and the oligomerization of ethyl lactate, is suggested to be both an economically and efficient route to produce lactide with high yield (82%).

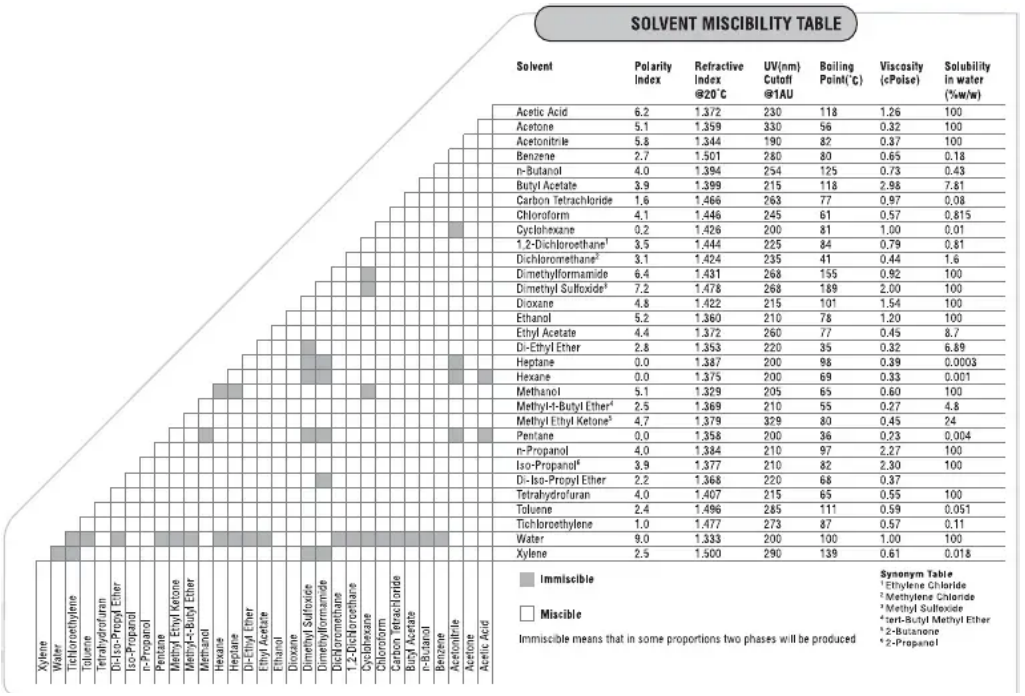


Scheme 1. Synthesis of PLA via alkyl lactate formation and ring-opening polymerization (image to the left).

High levels of contamination such as inorganic salt and other organic acids affect the final yield and optical selectivity. Crude lactic acid has to be purified before lactide forms, since the dimerization reaction of the alkyl lactate is reversible. Recovery of lactic acid from the fermentation broth cannot be performed via evaporation or distillation, considering the compound is nonvolatile and undergoes oligomerization at higher concentrations and temperatures (Upare, P. P., et al. 2012). Lactic acid, its derivatives and the undesired inorganic salts are both polar, making neither a solvent of high or low polarity suitable. Semipolar or a more correct term, dipolar, aprotic solvents, are thought to be a ‘’middle ground’’ of these issues. These solvents are

applicable in a large variety of reactions and serve as mediums. They do not form hydrogen bonds, but may cause a polarity in nonpolar molecules (Ashenhurst, J., 2020).

Butanol (Stepan, D. J. et al., 2001; Chawong, K., Rattanaphanee, P., 2011) and ethyl acetate (Hu, Y. et al., 2017) have been proposed as a good extraction solvent for ethyl lactate and looking at the polarity index of both solvents (FIG.4), both seem like great semipolar candidates. However following the well known principle of 'like dissolves like', similar molecules will dissolve in similar, a theory of ethyl acetate being the more favorable solvent is examined due to its similar molecular structure as ethyl lactate (Ethyl Lactate. n.d.)



Solvent	Polarity Index	Refractive Index @20°C	UV(nm) Cutoff @1AU	Boiling Point(°C)	Viscosity (cPoise)	Solubility in water (%w/w)
Acetic Acid	6.2	1.372	230	118	1.26	100
Acetone	5.1	1.359	330	56	0.32	100
Acetonitrile	5.8	1.344	190	82	0.37	100
Benzene	2.7	1.501	280	80	0.65	0.18
n-Butanol	4.0	1.394	254	125	0.73	0.43
Butyl Acetate	3.9	1.399	215	118	2.98	7.81
Carbon Tetrachloride	1.6	1.466	263	77	0.97	0.08
Chloroform	4.1	1.446	245	61	0.57	0.815
Cyclohexane	0.2	1.426	200	81	1.00	0.01
1,2-Dichloroethane[1]	3.5	1.444	225	84	0.79	0.81
Dichloromethane[2]	3.1	1.424	235	41	0.44	1.6
Dimethylformamide	6.4	1.431	268	155	0.92	100
Dimethyl Sulfoxide[3]	7.2	1.478	268	189	2.00	100
Dioxane	4.8	1.422	215	101	1.54	100
Ethanol	5.2	1.360	210	78	1.20	100
Ethyl Acetate	4.4	1.372	260	77	0.45	8.7
Di-Ethyl Ether	2.8	1.353	220	35	0.32	6.89
Heptane	0.0	1.387	200	98	0.39	0.0003
Hexane	0.0	1.375	200	69	0.33	0.001
Methanol	5.1	1.329	205	65	0.60	100
Methyl-t-Butyl Ether[4]	2.5	1.369	210	55	0.27	4.8
Methyl Ethyl Ketone[5]	4.7	1.379	329	80	0.45	24
Pentane	0.0	1.358	200	36	0.23	0.004
n-Propanol	4.0	1.384	210	97	2.27	100
Iso-Propanol[6]	3.9	1.377	210	82	2.30	100
Di-Iso-Propyl Ether	2.2	1.368	220	68	0.37	
Tetrahydrofuran	4.0	1.407	215	65	0.55	100
Toluene	2.4	1.496	285	111	0.59	0.051
Tichloroethylene	1.0	1.477	273	87	0.57	0.11
Water	9.0	1.333	200	100	1.00	100
Xylene	2.5	1.500	290	139	0.61	0.018

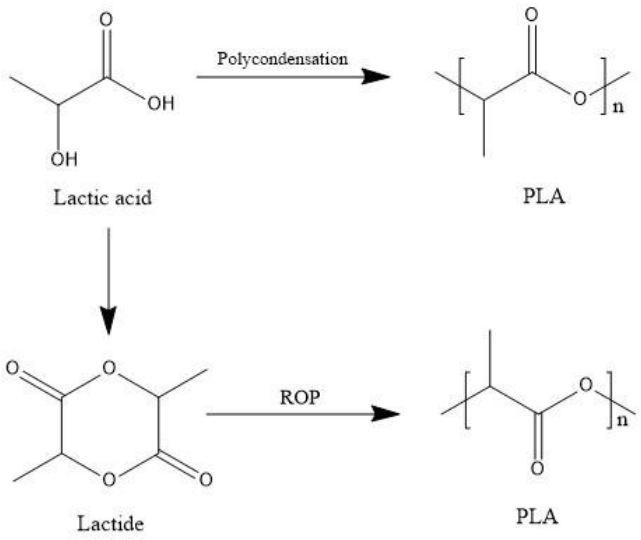
Figure 2. Solvent Miscibility Table (Pham, D. n.d.)

2.2 Formation of lactide

Lactide is a cyclic dimer of lactic acid and gets synthesized in two steps. Firstly, lactic acid needs to undergo a polycondensation, forming an oligomer of lactic acid. This oligomer gets depolymerized with the usage of a catalyst to generate lactide. Great amount of energy is required for this reaction to occur as temperature needs to reach above 200°C and the reaction may result in a lower molecular-weight product if contaminants are present (Itzinger, R., et al, 2020). The costs of production are considered high, thereby research is being done to improve the methods for the synthesis of lactide. There have been attempts to make lactide in a one-step reaction by condensation and dimerization of lactic acid, while controlling the formation of oligomers. This was achieved by using metal organic frameworks such as a zeolite catalyst (Upare, P.P, et al, 2012). Other studies have altered the catalysts used. A patent details, among other things, how lactide may be produced with zinc oxide as catalyst, which allows for more efficient lactide production while using less energy (Hu, Y, et al, 2016). The increased synthesis efficiency is due to the fact that zinc oxide is a novel catalyst, meaning it has a bigger surface area, allowing it to integrate with lactic acid. The low energy consumption is also attributed to the high catalytic effectiveness of zinc oxide, which helps the depolymerization and purification of the lactide, resulting in reduced synthesis at lower temperatures and times. Although the most common catalyst used in the formation of lactide is stannous octoate and can be found in a lot of previous studies and patents.

2.3 Polylactic acid synthesis via lactide formation

PLA can be manufactured in two different ways, by ring-opening polymerization of lactide or polycondensation of lactic acid (Lee, C., Hong, S., 2014). Through polycondensation PLA is made when the carboxyl and hydroxyl groups of lactic acid are polycondensed, resulting in water byproduct (FIG.5). Polycondensation is the less common method in industrial scale since the synthesis produces low molecular weight PLA due to the fact that it is hard to remove water from the viscous solution. Ring opening polymerization is more commercially used because of its ability to yield high molecular polymers. Lactic acid is condensed into a low-molecular weight PLA or pre-polymer. An initiator, such as a metal catalyst containing tin, titanium or aluminium is employed to convert them into a mixture of lactide stereoisomers, which is further filtered by vacuum distillation (Hu, Y., et al, 2015).



Scheme 2: Scheme over the formation of polylactic acid via polycondensation and ring opening polymerisation (ROP).

2.4 NMR

Nuclear magnetic resonance spectroscopy (NMR) was utilized to determine the composition and conversion of the samples. NMR operates via electromagnetic frequencies and magnetic fields to study molecular structure by converting it into a spectrum that can be deciphered down to the atomic level (Emsley, J.W, 1999). Each molecule has peaks in its spectrum at particular locations, and the area of a peak is proportional to the molecule's concentration. This study utilized ^{1}H NMR for the determination of conversion and purity of the samples.

When analyzing the results of the NMR spectras, other works and research of PLA and lactide was utilized for reference values and the following spreadsheet (see *Table 3*) is the result and interpretation of the articles that were researched. All numbers are defined in ppm in respect to the solvent, chloroform ($CDCl_3$) (Almius & Larsson, 2020; Xiao, G. et al., 2011; Rodríguez-Tobías, H. et al., 2015).

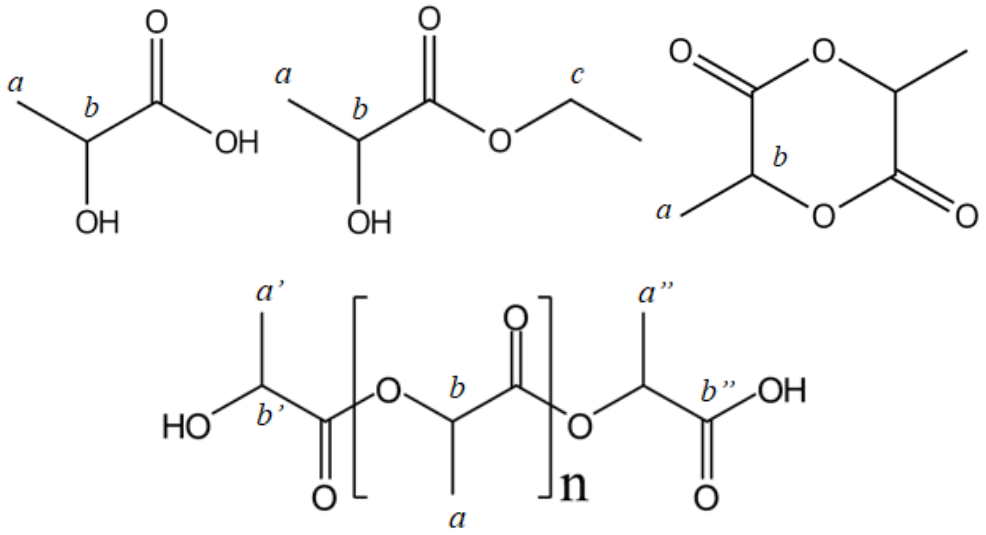


Figure 3. Atom places for each molecule in Table x. Lactic acid (top left), ethyl lactate (top middle), lactide (top right) and PLA (bottom).

***Table 1*: ^{1}H NMR reference values for the compounds showcased in Figure 2.**

Lactic acid	***a* (CH_3)**	***b* (CH)**	
Value (ppm)	1.3-1.4	4.36-4.38	
Ethyl lactate	***a* (CH_3)**	***b* (CH)**	***c* (CH_2)**
Value (ppm)	1.3-1.4	4.29	4.21
Lactide	***a* (CH_3)**	***b* (CH)**	
Value (ppm)	1.65-1.68	5.02-5.07	
PLA	***a* (CH_3)**	***b* (CH)**	***b* + *b'***
Value (ppm)	1.4-1.6	5.1-5.3	4.3-4.5

2.5 Microwave Irradiation & IR moisture analyzer

Microwave irradiation is a non-conventional heating technology that can be employed in chemical reactions (Pandey, A., Aswath, P.B., 2009). In some circumstances, this approach is favored since it reduces reaction time and uniformly heats the material. The microwave method works by oscillating the molecules of a bipolar solvent or a solvent containing ions in a microwave field. The microwave energy is absorbed by the molecules, which causes the sample to heat up (Dahiye, M.S., et al., 2018). Many studies have shown that microwave irradiation is far more efficient than conventional heating in the synthesis of PLA (Bakibaev, A.A, et al, 2015; Nagahata, R., et al., 2007). In this study, microwave irradiation was used to examine reaction routes and circumstances.

2.6 IR moisture analyzer

The dry content of LA_W was determined using an IR moisture analyzer, which calculates the percentage of dry matter. A small layer of the sample is put over a weighing pan, which is subsequently heated using both IR and convection heating, analyzing evaporated moisture over time.

A drying curve can then be used to graphically represent the percentage of dry content over time.(Kowalska, M., et al, 2018)

3. Experimental

Lactic acid solution, LA_W (~10%, RISE Processum), Ethanol (99.98%, Solveco), *p*-Toluenesulfonic acid (≥98.95%, Sigma-Aldrich), Ethyl acetate (100%, WR Chemicals), Tin(II) 2-ethylhexanoate (92.5-100.0%, Sigma-Aldrich). 3-methyl-1-butanol (98%, Riedel-de Haën). Lactic acid (~100%, Sigma-Aldrich) was used for calibration. Chloroform-d (~100%, Sigma-Aldrich) was used as a solvent for ^{1}H NMR spectroscopy. Process flow diagrams (PFD) were done using the website *online.visual-paradigm.com*.

3.1 Method

3.1.1 Determination of percentage of lactic acid in LA_W

Dry content was determined using an IR moisture analyzer. 1 g of LA_w was placed on the weighting unit of the device that heats and dries the sample, while the dry content is measured every minute.

3.1.2 Purification and recovery of lactic acid by desorption on AC

100g of the provided lactic acid solution, LA_w (~10 g/L) was centrifuged for 30 min for biomass-separation. The centrifugation step was added due to no prior knowledge of the pre-treatment of LA_w. The centrifuged LA_w and 16.36 g AC was added in a beaker, stirred and heated to 30°C for 6h using a magnetic stirrer. Vacuum filtration was performed. The recovered charcoal was added into a flask containing 200ml acetone for desorption and was left in a stationary state overnight at room temperature. The mixture was filtered and washed with acetone twice. Removal of acetone was performed using a rotary evaporator.

3.1.3a Synthesis of alkyl lactate

2.5 g lactic acid (10%; 20%; 50%; 100%), 4 ml ethanol, 100mg *para*-toluenesulfonic acid was added in a flask and heated to 80°C for 4h with a magnetic stirrer. Solvent was removed by a rotary evaporator.

3.1.3b Direct synthesis of alkyl lactate from LA_w

50% of LA_w was evaporated to achieve a concentration of ≥20%. 98 mmol ethanol and 0.58 mmol *para*-toluenesulfonic acid was added for every gram of LA in LA_w. Removal of solvent was performed using a rotary evaporator. Ethyl acetate was added in the flask. The liquid was decanted from the salt and later evaporated to achieve the product.

3.1.4a Formation of lactide

23.6 g of ethyl lactate and 0.14 g of stannous octoate were added into a pear-shaped flask, equipped with a stirrer, a condenser, a thermometer and a tube introducing nitrogen gas. Mixture was distilled and stirred at 160°C and pressure at ordinary pressure to 24mmHg under a nitrogen flow for 2 hours. The reaction liquid obtained was distilled while keeping a pressure of 24 mmHg and a liquid temperature of 200°C for 1h to obtain the product. The reduced pressure was obtained using a water aspirator.

3.1.4b Formation of lactide, ZnO as catalyst

50 g lactic acid was mixed with 1 g zinc oxide. The mixture was stirred at 130°C for 3 h for removal of water formed in the reaction. The temperature was increased to 220°C, and distilled for 1 h under a nitrogen atmosphere. The reduced pressure was obtained using a water aspirator.

3.1.5 Microwave-assisted synthesis of PLA

The reactions took place in a G30 reaction glass vial. The examined variables were the concentration of catalyst:co-catalyst, temperature and time. Temperature varied between 160-220°C and time, 10-20 min.

3.2 Measurements

The Agilent NMR system was utilized and operated at 400MHz to record the ^{1}H NMR spectras. The samples were dissolved in Chloroform-d, $CDCl_3$ and the spectrums were recorded at 298 K. The chemical shifts (δ) were expressed in ppm with regards to the $CDCl_3$ signals at 7.26 ppm (^{1}H). Moisture content of LA_w was determined by using Infrared Moisture Meter. The Anton Paar Monowave 200 was utilized as an alternative heating method using microwaves.

3.3 Yield calculation

Calculation of yield in this report was done by following the Towler and Sinnott's definition of yield.

$$Yield = Conversion \times Selectivity$$

Conversion was calculated by looking at the ^{1}H NMR spectra and observing how much of the unique peak of the start material had changed after the reaction. Selectivity looks at the amount of start material that has been converted into product and byproducts and quantifies the amount within that conversion. Multiply these values and the yield of the reaction has been determined.

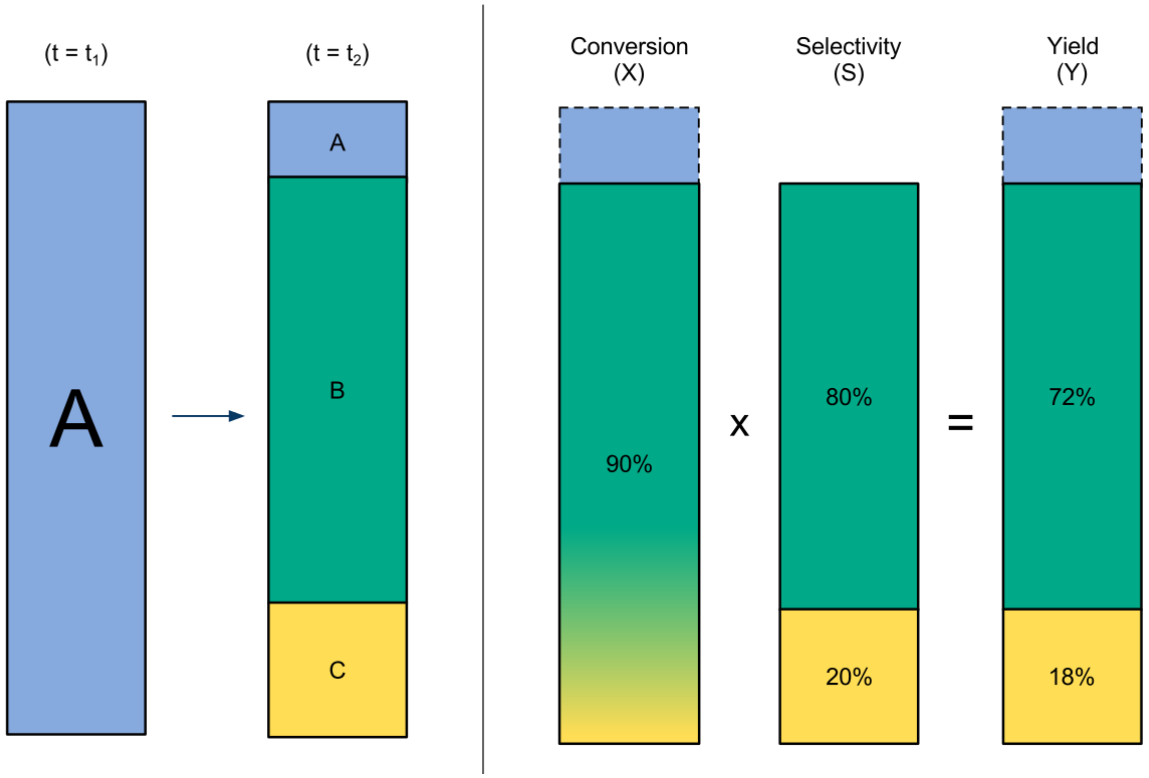


Figure 4. Illustration of the calculation of yield.
File:Conversion, Selectivity and Yield.svg. (n.d). Retrieved from: *https://commons.wikimedia.org/w/index.php?title=File:Conversion,_Selectivity_and_Yield.svg&oldid=456542450*.

4. Results and Discussion

4.1 Determination of percentage of lactic acid in LA_w

The dry content of LA_w was determined using an IR moisture analyzer and was estimated to be 12%. Although the IR analysis estimated the dry content to be 12%, it is probably not representative of the lactic acid content in LA_w. The estimate includes salts and other impurities from the manufacturing process. 12% is the theoretical maximum percentage assuming 100% of the dry content is lactic acid.

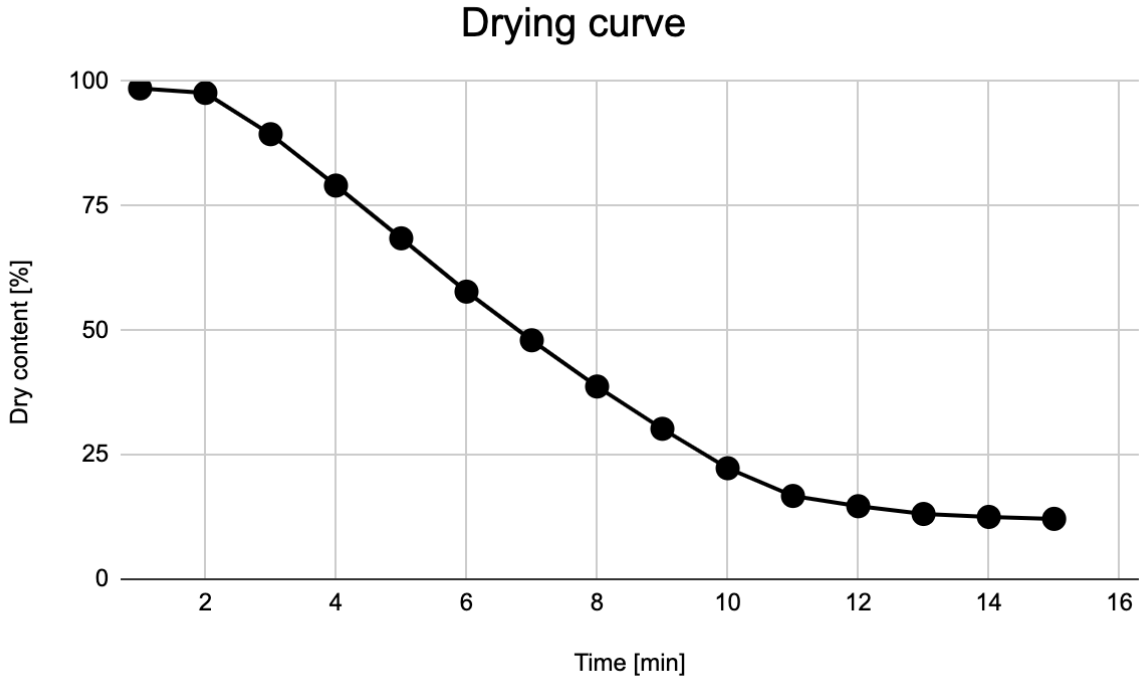


Figure 5: Drying curve of LA_w.

4.2 Recovery of lactic acid from sludge

An average was determined for both methods using either new AC or reused AC (Table 2). When extracting the lactic acid and evaporating the solvents, the dry content will increase and will most likely lead to an oligomerization. Assuming the lactic acid content was ~10%, an approximation of the yield was performed.

The process of using new activated charcoal resulted in a 100% yield. It is important to note that a yield over 100% should not be possible, these results are probably due to impurities still in the product such as other carboxylic acids, organic and inorganic compounds. The method of using reused charcoal resulted in a lower degree of polymerization and yield. This was expected to occur since a guaranteed, complete removal of reactants from the previous experiments is quite difficult to achieve, but the reasoning of this experiment was to observe the difference using only simple techniques.

Table 2. Purification of lactic acid via desorption of activated charcoal (AC).

AC	DP	Yield (%)
Unused	~20	100-107.3
Reused*	~13	~81

* The AC from previous experiments was reused.

4.3 Synthesis of ethyl lactate

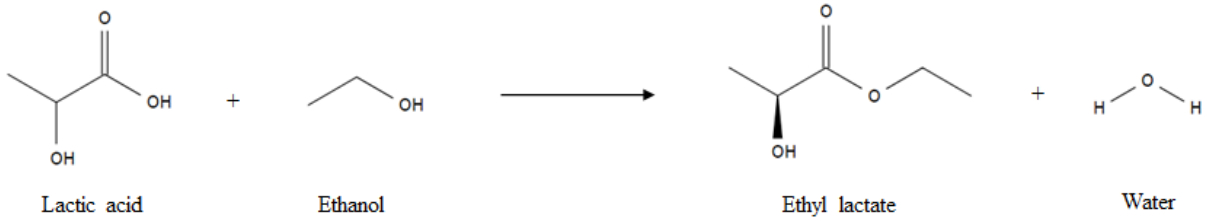


Figure 6. The chemical reaction of synthesis of ethyl lactate.

The esterification of pure lactic acid showcased excellent conversion to ethyl lactate (Table 3). It was observed that after a percentage of ~20%, the conversion plateaued. This is not surprising, since it has been shown that polymerizing the monomer first is necessary for the reaction to occur and when a solution has a lactic acid content of ≥20%, the monomer goes through a spontaneous polymerization. It is important to note that despite the seemingly lower yield and conversion at 100% lactic acid concentration, the sample had less water and thereby less shifting and overlapping in the NMR €spectrum. For synthesis of ethyl lactate, a percentage of 20% lactic acid is necessary.

Table 3. Synthesis of ethyl lactate using lactic acid (>98%).

Lactic acid conc.	10%	20%	50%	100%
Conversion (%)	4.941	80.20	87.20	83.90
Yield (%)	-	62.95	75.27	69.20

Reaction conditions: ~10-100% lactic acid 2.5g, 99.98% ethanol 4ml, *p*-TsOH 100mg, temperature 80°C, time 2 h.

With this knowledge, five experiments were performed using the impure lactic acid, LA_W, (Table 4) by reducing and evaporating to achieve concentration of ~20%. Small amount of product was used in Experiment **1** to quickly confirm if the conversion using LA_w was possible. In Experiment **2**, the process was scaled up approximately 10x.

Table 4. Direct synthesis of alkyl lactate from LA_w

Experiment	Conversion (%)	Yield (%)
1	45.4	[inconclusive]
2	66.7	33.5
3	24.8	20.1
4	-	0.8

Molar ratio: LA_w (in respect to LA) : ethanol : *p*-TsOH [9.6:149.5:1], temperature 80°C, time 2 h.

Experiment **1** showcased poor conversion and yield. Experiment **2** was still a small sample, but it served as an early indication. The water content is an important factor and combined with the untreated impurities, the synthesis of ethyl lactate was not as successful as hoped. Salts and the other unknown substances in LA_w is the probable inhibitor of the reaction. Regardless of the first two results, additional experiments were conducted on a larger scale to confirm the theory. A plausible theory as to why the yield in the third experiment was lower than the previous two experiments, is that as the sample size increases, the amount of impurities increases as well. As seen in Experiment **4** performed with an even larger scale gave an even lower yield (0.8 %). When adding ethyl acetate to

separate the impurities from the ethyl lactate, the solvent might have difficulties penetrating the viscous sludge at the bottom of the flask, making it difficult to adsorb more ethyl lactate.

4.4 Synthesis of lactide

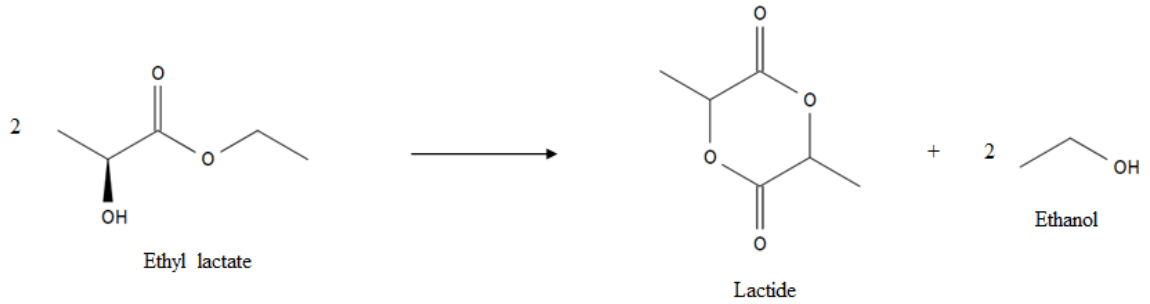


Figure 7. Chemical reaction of lactide formation, when $Sn(Oct)_2$ was used as a catalyst.

The experiments using $Sn(Oct)_2$ as a catalyst resulted in poor yield and conversion, however when the reaction was performed under inert gas, the yield improved (Table 5). The reason the conversion is significantly higher is most likely due to ethyl lactate being hydrolyzed back into lactic acid. If the reaction does not have the correct conditions, such as low pressure and inert atmosphere, ethanol will still be present and the moisture present in the air will hydrolyze the reaction and will prohibit the lactide from forming.

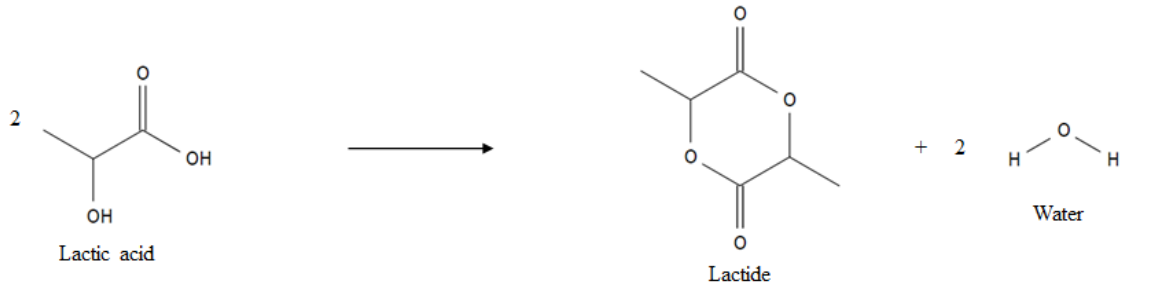


Figure 8. Chemical reaction of lactide formation, ZnO as a catalyst.

The results of using zinc oxide as a catalyst was more promising than using stannous octoate. Ethyl lactate has the risk of converting back into lactic acid during the reaction, whereas in the synthesis of zinc oxide, the lactic acid can only undergo oligomerization or forward with the reaction. This reaction using lactic acid as start material, is easier to conduct and produces less unwanted products. Additional research and testing using different parameters should be pursued using zinc oxide as catalyst. The reaction showcased some promise and the potential of being equal as a catalyst to $Sn(Oct)_2$.

Table 5. **Conversion and yield of lactide based on reactant, catalyst and experiment.**

Reactant	Catalyst	Conversion (%)	Yield (%)
Ethyl lactate	$Sn(Oct)_2$	30.96	3.01
Ethyl lactate*	$Sn(Oct)_2$	51.8	0.89
Ethyl lactate	$Sn(Oct)_2$	27.71	6.04
Lactic acid	ZnO	43.56	8.0
Lactic acid	ZnO	43.31	3.27

*Reaction was not conducted in an inert atmosphere.

4.5 Microwave-assisted synthesis of PLA

PLA was produced through the synthesis of lactic acid, as evidenced by ^{1}H NMR. Several temperatures were tried, with 180°C proving to be the most effective. Conversion increased up to 180°C, but started decreasing above that temperature (Table 6). PLA degrades at higher temperatures, which could explain the outcome. Ethyl lactate was also utilized to make PLA (Table 7). Although NMR revealed the production of PLA, it resulted in significantly lower conversions (>10%) than when LA was utilized (32 % at 180 °C). Using ethyl lactate at various temperatures shows that conversion increases up to 190°C before decreasing. Since we did not test 190°C for lactic acid, it is possible that this is the greatest temperature before the polymer will degrade.

Although PLA may be indicated in NMR, the conversion rate was not high enough for our method to be effective. This could change if some of the parameters were adjusted, as past research and literature have indicated higher conversions. An example is that PLA formation is frequently produced under low pressure in the literature reviewed which we did not use. Despite the low conversion rate, the microwave was the cheapest, fastest, and simplest approach, compared to a more expensive process with a higher yield. Synthesis of PLA according to conventional heating can take several hours depending on the scale, but through microwave synthesis you can produce PLA at a much faster rate. In this experiment, PLA was synthesized in 30 minutes. Lactic acid is more efficient than ethyl lactate since it provides better conversions. Previous PLA methods often start with lactic acid and less frequently with ethyl lactate, implying that the same approach may not be applied for the two different starting materials which could also explain the differences in outcomes when using lactic acid and ethyl lactate as reactants.

Table 6. **Microwave-assisted PLA synthesis using LA**

T (°C)	Conversion (%)	Appearance
180	32	Yellow, slight increase in viscosity
200	28	Slight increase in viscosity.
220	24	Same/similar appearance

Reaction conditions: Molar ratio, 100:3:3. LA:$Sn(Oct)_2$:isoamyl alcohol, time 20 min.

Table 7. **Microwave-assisted PLA synthesis using ethyl lactate**

T (°C)	Conversion (%)	Appearance
170	6.4	Color and viscosity similar to milk
190	7.1	Increase in viscosity
210	7.0	Increase in viscosity, similar to school glue

Reaction conditions: Molar ratio, 100:3:3, EtLA:$Sn(Oct)_2$:isoamyl alcohol, time 20 min.

4.6 Process Flow Diagram (PFD) and cost of chemicals

Since one of the objectives of this thesis was to produce 5g of lactide and calculate the total cost of the materials, calculations are done backwards with the lactide reaction to the purification of lactic acid solution. When calculating the costs of the chemicals, bulk sizes are chosen and later divided to achieve a unit of *kr/kg*. The tables below are based upon this report's results. Every value of a product is based on the actual amount of product based on yield from this report. Calculations are not based upon the crude product.

The costs of the chemicals can be scalable linearly, although not with the solvents. The solvents in this process (ethanol, acetone and ethyl acetate) can be reintroduced back into the system in their respective step via a recycle stream to lower the costs and waste management. Activated charcoal can be utilized multiple times if undergoing steam-, solvent-, chemical- or thermal regeneration with the aim of removing the adsorbents on its surface. The cost of the different methods of regeneration could not be found, thereby the price of regeneration was not included and the estimations were done as if only new activated charcoal was introduced every batch.

Formation of Lactide.

It is important to have an appropriate temperature and pressure since evaporation of the ethanol is desired, not of the ethyl lactate (Table 8).

Table 8. **Cost of producing 5 grams lactide, $Sn(Oct)_2$ as catalyst.**

Material	EtLA	$Sn(Oct)_2$	Product
Weight/Volume	23.6 g	0.14 g	0.13g
Cost (kr/kg)*	-----	2 050	
Theoretical tot. weight (or volume)	930.31 g	5.52 g	5 g
Theoretical tot. cost (kr)	=	11.04	

* Price taken from sigmaaldrich.com

Synthesis of Ethyl Lactate

This reaction step is fairly simple with relatively low temperatures and not energy-demanding, compared to some of the other reaction steps where temperatures reach above 200°C. The amount of ethyl lactate produced was determined in *Table 8*. The cost of producing ethyl lactate was determined in the table below (Table 9).

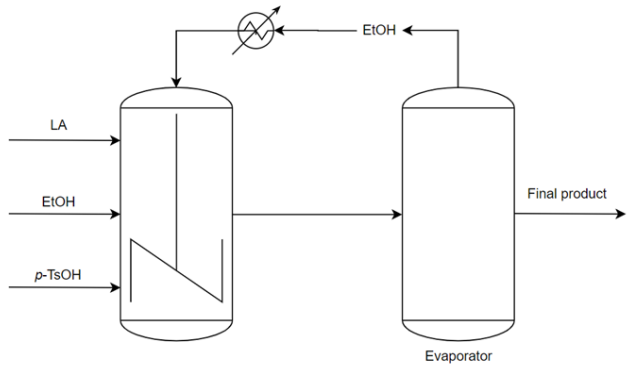


Figure 9. Process flow diagram over the suggested method of synthesis of ethyl lactate (see 3.1.2).

***Table 9.* Production of ethyl lactate to produce 930.31 g.**

Material	LA	EtOH	*p*-TsOH	Product
Weight/Volume	2.5 g	4 ml (3.156 g)	100 mg	2.81 g
Cost (kr/kg or L)	---	12.353*	219.333**	
Theoretical tot. weight (or volume)	829.15 g	1336.81 ml (1046.72 g)	33.11 g	930.31
Theoretical tot. cost (kr)	=	16.51	7.26	= 23.77

* Price retrieved Jun, 3, from: globalpetrolprices.com/Sweden/ethanol_prices/
** Price retrieved from: sigmaaldrich.com

Purification and recovery of lactic acid

Based upon the method used in 3.1.1, a design of PFD was made. The method utilized in a laboratory scale is going to differentiate from an industrial scale, however the steps seem simple and possible to scale up with little to no difficulty. Decreasing pressure and/or higher temperature are a possibility if a higher desorption rate is desired.

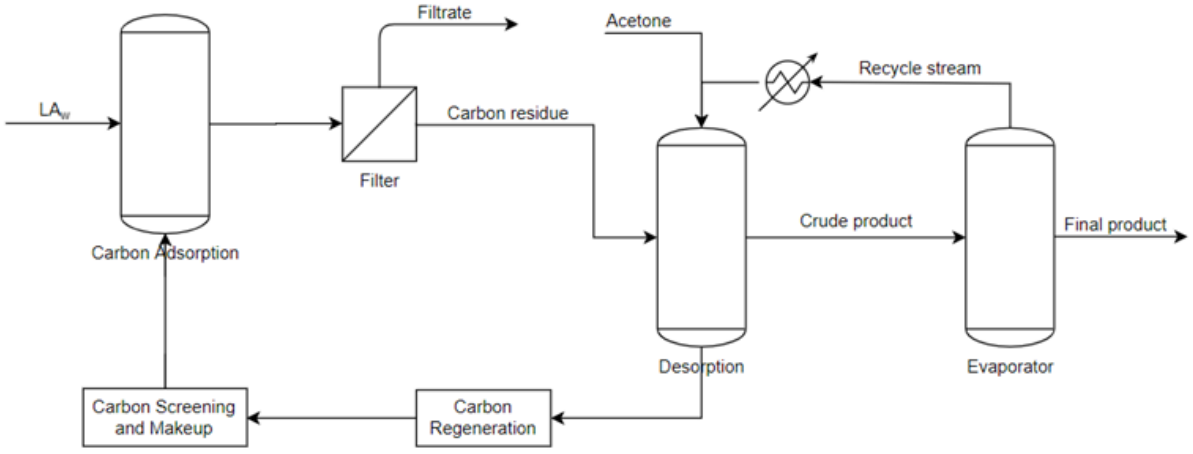


Figure 10. Process flow diagram over the suggested method of purification and recovery of lactic acid (see 3.1.1)

Table 10. **Purification of lactic acid from LA_w to produce 829.15 g lactic acid.**

Material	LA_w	Acetone	Activated carbon	Product
Weight/Volume	100 g	200 + 50 ml	16.36 g	10,76g
Cost (kr/kg or L)*	---	34.95	47.92	
Theoretical total weight/volume	7,71 kg	19.26 L	1260,6 g	829,15
Theoretical tot. cost (kr)	=	673,137 +	60,41 =	733,55

* Price retrieved from https://www.ikaros.net/sv/iks/aceton-200-l, June, 10.

Table 11. **Cost of producing lactide, ZnO as catalyst.**

Material	LA**	ZnO	Product
Weight/Volume	50g	1g	2.8
Cost (kr/kg or L)*		839.2	
Theoretical total weight/volume	89,28	1.79g	5 g
Theoretical tot. cost (kr) =	78,99 +	1.5 =	80,49

* Price retrieved from https://www.merckmillipore.com/SE/en/product/Zinc-oxide,MDA_CHEM-108849, Dec, 2021 .
** Assuming the lactic acid comes from the purification of the lactic acid step.

By calculating the costs of every step of the process, it is clear that using our methods may not have been economically beneficial. Most of the cost is due to the amount of acetone in the purification step but as stated before, the acetone can be recycled by evaporation and reintroduced into the process. These calculations are a very rough estimate of the cost of the process. Although many factors in the calculations were not or could not be taken into consideration, this chapter was a good exercise and overview on how expensive and the vast amount of chemicals that are necessary to produce the product.

Table 12. **Total cost of materials for production of lactide, 5 g.**

Chemical	Acetone	AC	EtOH	*p*-TsOH	$Sn(Oct)_2$
Cost of reaction stage (kr)					
Purification of LA	673.14	60.41			
Ethyl lactate			16.51	7.26	
Lactide, *Sn(Oct)₂*					11.04
Tot. cost (kr), *Sn(Oct)₂*	=	768.36 kr / 5g		= 153 672 kr/kg	
Tot. cost (kr), *ZnO*	=	735.05 kr / 5g		= 147 010 kr/kg	
Cost of commercial lactide*				= 26 087 kr/kg	

* Price retrieved from:
https://www.fishersci.com/shop/products/l-lactide-98-thermo-scientific-1/AAL0903114#?keyword=l-lactide, Dec, 2021.

5. Conclusion

The main goal of this thesis was the synthesis of lactide using a residual product from the pulp industry, which had a lactic acid content estimated at ~10%. This was performed by a series of syntheses with varying results. The impure lactic acid solution, LA_W, underwent a purification step using activated charcoal and acetone extraction with a yield close to ~100% . The synthesis of ethyl lactate, the dry content of lactic acid, has to be ≥20% for the reaction to be successful, achieving a yield of ≥93%. The same reaction was tested using a lactic acid solution containing impurities and this resulted in a much lower yield of 34%. A probable theory is the impurities made the extraction more difficult and for the solvent to penetrate the sludge. Two different methods of lactide synthesis were investigated and zinc oxide as catalyst, was the superior method of the two. It is important to acknowledge that inert conditions and low pressure are significant for the production of lactide and this was difficult to achieve in the facilities used.

Lactide is used as a starting material for the production of polylactic acid (PLA) and in this study, a microwave assisted synthesis of PLA is promising due to higher reaction rate compared to conventional heating. A cost estimate was calculated based upon the results of this study. The cost estimate suggests that producing 5 g of lactide costs 735.05kr when using zinc oxide as catalyst or 768.36kr when using stannous octoate.

6. Future work

There is great potential of polylactic acid becoming a more environmentally-friendly alternative to conventional polymer plastics, or even replacing it altogether. Although there is much research surrounding the topic of synthesis of polylactic acid and lactide, the research might not have yet reached its point of reassurance that it is economically favorable compared to the fossil-based plastics. The demand and interest for biodegradable and environmentally-friendly plastic has increased over the years, however the process and subject is still unknown or incomprehensible to most of the public and thus prevents any interest towards PLA/lactide from the public from increasing.

With the current research, the process might not be beneficial to produce. The extraction from LA_w, can result in other compounds being investigated and further researched upon. For example the purified LA_w with activated coal is not used to synthesize ethyl lactate in this study, but it is something that may be studied further. Educating youths in upper secondary schools about the great potential polylactic acid and other bio-plastics has for being a promising alternative for fossil-based plastics, has the possibility of invoking ideas and innovation early for new methods and optimization of the production process, in terms of both financially and its sustainability.

7. References

Almius, Linnéa & Larsson, Jonas. Synthesis of Lactide with Varied Bases by Design of Experiments, via Azeotropic Distillation and Examine Potential Use of Molecular Sieves, 2020, hdl.handle.net/20.500.12380/301375.

Ashenhurst, J. (2020, February 12). Polar Protic? Polar Aprotic? Nonpolar? All About Solvents. Retrieved from: https://www.masterorganicchemistry.com/2012/04/27/polar-protic-polar-aprotic-nonpolar-all-about-solvents/

Chawong, K. , Rattanaphanee, P. (2011). 'n-Butanol as an Extractant for Lactic Acid Recovery'. World Academy of Science, Engineering and Technology, Open Science Index 56, International Journal of Chemical and Molecular Engineering, 5(8), 733 - 736.

Cooney, D. O., Nagerl, A., & Hines, A. L. (1983). Solvent regeneration of activated carbon. Water Research, 17(4), 403-410. doi:10.1016/0043-1354(83)90136-7

Ethyl acetate. (2019, March 11). American Chemical Society. Retrieved May 10, 2021, from https://www.acs.org/content/acs/en/molecule-of-the-week/archive/e/ethyl-acetate.html

Ebben, A., Carlson, C. (2021). A Look at Activated Carbon Thermal Regeneration. Retrieved from: https://feeco.com/a-look-at-activated-carbon-thermal-regeneration/#:~:text=Regeneration%2C%20often%20referred%20to%20as,again%20function%20as%20an%20adsorbent

File:Conversion, Selectivity and Yield.svg. (2020, September 12). Wikimedia Commons, the free media repository. Retrieved 11:57, December 19, 2021 from https://commons.wikimedia.org/w/index.php?title=File:Conversion,_Selectivity_and_Yield.svg&oldid=456542450.

Foo, K., & Hameed, B. (2012). Microwave-assisted regeneration of activated carbon. Bioresource Technology, 119, 234-240. doi:10.1016/j.biortech.2012.05.061

Gao, M., Shimamura, T., Ishida, N., & Takahashi, H. (2011). PH-uncontrolled lactic acid fermentation with activated carbon as an adsorbent. Enzyme and Microbial Technology, 48(6-7), 526-530. doi:10.1016/j.enzmictec.2010.07.015

Guo, D., Shi, Q., He, B., & Yuan, X. (2011). Different solvents for the regeneration of the exhausted activated carbon used in the treatment of coking wastewater. Journal of Hazardous Materials, 186(2-3), 1788-1793. doi:10.1016/j.jhazmat.2010.12.068

Guo, Y., & Du, E. (2012). The Effects of Thermal Regeneration Conditions and Inorganic Compounds on the Characteristics of Activated Carbon Used in Power Plant. Energy Procedia, 17, 444-449. doi:10.1016/j.egypro.2012.02.118

Hu, Y., Kwan, T. H., Daoud, W. A., & Lin, C. S. (2017). Continuous ultrasonic-mediated solvent extraction of lactic acid from fermentation broths. Journal of Cleaner Production, 145, 142-150. doi:10.1016/j.jclepro.2017.01.055

Hu, Y., Daoud, W., Cheuk, K., & Lin, C. (2016). Newly Developed Techniques on Polycondensation, Ring-Opening Polymerization and Polymer Modification: Focus on Poly(Lactic Acid). Materials, 9(3), 133. doi:10.3390/ma9030133

Ikaros Cleantech AB. (n.d.). Aceton, 200 L. Retrieved June 10, 2021, from https://www.ikaros.net/sv/iks/aceton-200-l

Itzinger, R., Schwarzinger, C., & Paulik, C. (2020). Investigation of the influence of impurities on the ring-opening polymerisation of L-Lactide from biogenous feedstock. Journal of Polymer Research, 27(12). doi:10.1007/s10965-020-02339-3

John, R. P., Nampoothiri, K. M., & Pandey, A. (2007). Fermentative production of lactic acid from biomass: An overview on process developments and future perspectives. Applied Microbiology and Biotechnology, 74(3), 524-534. doi:10.1007/s00253-006-0779-6

Kang, L., Wang, W., & Lee, Y. Y. (2010). Bioconversion of Kraft Paper Mill Sludges to Ethanol by SSF and SSCF. Applied Biochemistry and Biotechnology, 161(1-8), 53-66. doi:10.1007/s12010-009-8893-4

Kowalska, M., Janas, S., & Woźniak, M. (2018). Innovative application of the moisture analyzer for determination of dry mass content of processed cheese. *Heat and Mass Transfer*, *54*(10), 3071–3080. https://doi.org/10.1007/s00231-018-2358-7

Kuokkanen, T., Nurmesniemi, H., Pöykiö, R., Kujala, K., Kaakinen, J., & Kuokkanen, M. (2008). Chemical and leaching properties of paper mill sludge. Chemical Speciation & Bioavailability, 20(2), 111-122. doi:10.3184/095422908x324480

Marques, S., Santos, J. A., Gírio, F. M., & Roseiro, J. C. (2008). Lactic acid production from recycled paper sludge by simultaneous saccharification and fermentation. Biochemical Engineering Journal, 41(3), 210-216. doi:10.1016/j.bej.2008.04.018

Möllersten, K., Gao, L., Yan, J., Obersteiner, M. (2004): Efficient energy systems with CO2 capture and storage from renewable biomass in pulp and paper mills, Renewable Energy, vol 29, 1583-1598

Pham, D. (2004, October 23). Solvent miscibility table. Academia. Retrieved from: https://www.academia.edu/8932829/Solvent_miscibility_table

Rodríguez-Tobías, Heriberto, et al. “One-Pot Formation of ZnO-Graft -Poly(d ,l -Lactide) Hybrid Systems via Microwave-Assisted Polymerization of d ,l -Lactide in the Presence of ZnO Nanoparticles.” Macromolecular Chemistry and Physics, vol. 216, no. 15, 2015, pp. 1629–1637., doi:10.1002/macp.201500171.

Stepan, D. J., Olson, E. S., Shockey, R. E., Stevens, B. G., & Gallagher, J. R. (2001). Recovery Of Lactic Acid From American Crystal Sugar Company Wastewater. doi:10.2172/788118

Sun, K., Jiang, J., & Xu, J. (2009). Chemical Regeneration of Exhausted Granular Activated Carbon Used in Citric Acid Fermentation Solution Decoloration. Bulletin of the Chemical Society of Ethiopia, 23(1). doi:10.4314/bcse.v23i1.21295

Sweden ethanol prices, 29-Nov-2021. (n.d.). GlobalPetrolPrices.Com. Retrieved June 3, 2021, from https://www.globalpetrolprices.com/Sweden/ethanol_prices/
Sweden/ethanol_prices

Takano, M., & Hoshino, K. (2016). Lactic acid production from paper sludge by SSF with thermotolerant Rhizopus sp. Bioresources and Bioprocessing, 3(1). doi:10.1186/s40643-016-0106-8

Tran, H. & Vakkilainen, E. (2016). THE KRAFT CHEMICAL RECOVERY PROCESS. Retrieved from:
https://www.tappi.org/content/events/08kros/manuscripts/1-1.pdf

Trä och träindustrin - världens sjätte största producent. (n.d.). Retrieved April 8th, 2021, from: https://www.skogssverige.se/tra-och-traindustrin-varldens-sjatte-storsta-producent

Upare, P. P., Hwang, Y. K., Chang, J., & Hwang, D. W. (2012). Synthesis of Lactide from Alkyl Lactate via a Prepolymer Route. Industrial & Engineering Chemistry Research, 51(13), 4837-4842. doi:10.1021/ie202714n

Xiao, Guoqi, et al. “Bulk Ring-Opening Polymerization (ROP) of L-Lactide Catalyzed by Ni(Ii) and Ni(Ii)-Sm(Iii) Complexes Based on a Salen-Type Schiff-Base Ligand.” Polym. Chem., vol. 2, no. 3, 2011, pp. 659–664., doi:10.1039/c0py00385a.

Zinc oxide. (n.d.). Merck. Retrieved December 1, 2021, from https://www.merckmillipore.com/SE/en/product/Zinc-oxide,MDA_CHEM-108849

Appendices

Appendix A: ^{1}H NMR spectras - Purification of lactic acid from LA_w

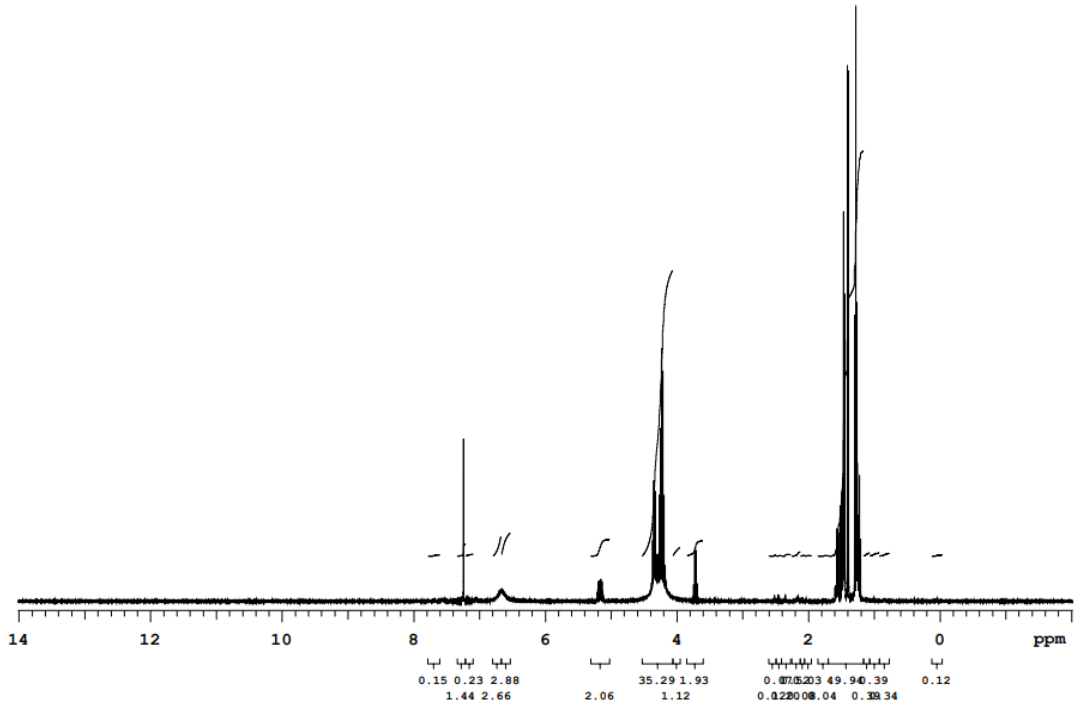


FIGURE A.1 ^{1}H NMR spectra *Purification of lactic acid from* $LA_{w,}$ new AC

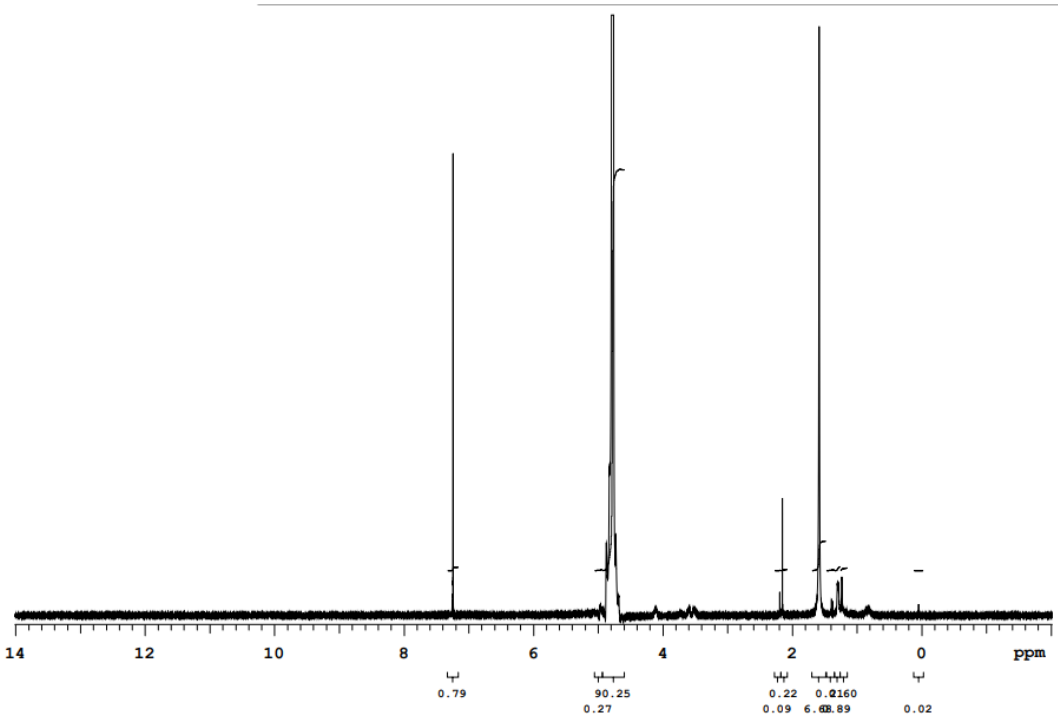


FIGURE A.2 ^{1}H NMR spectra *Purification of lactic acid from* $LA_{w,}$ new AC (2)

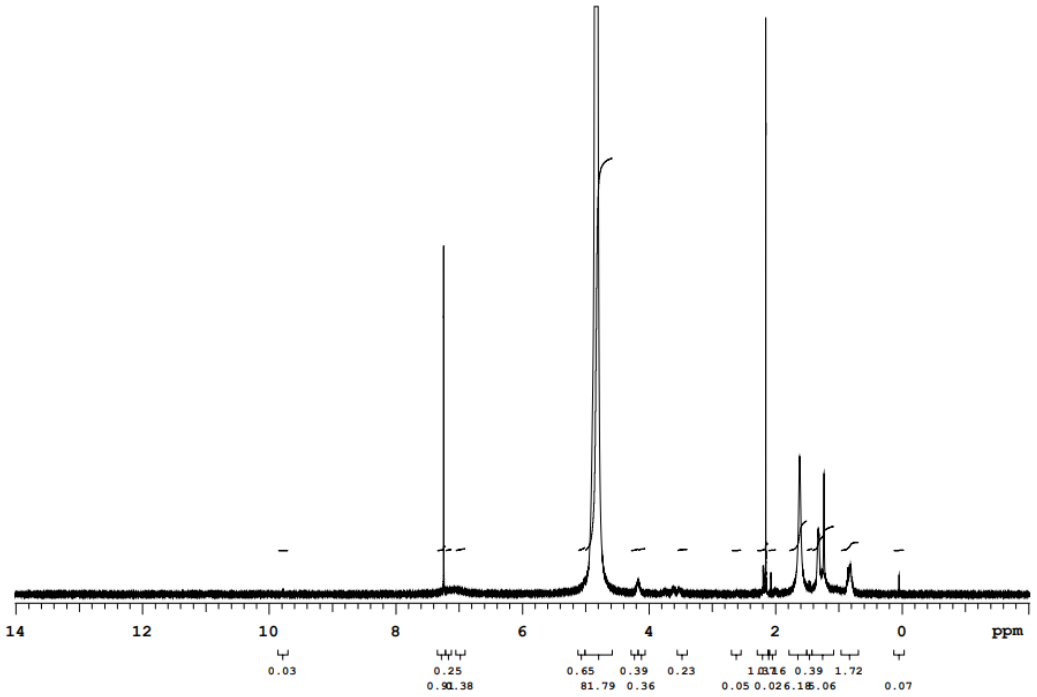


FIGURE A.3 ^{1}H NMR spectra *Purification of lactic acid from* $LA_{w,}$ reused AC from (2)

Appendix B: ^{1}H NMR spectras - Synthesis of ethyl lactate

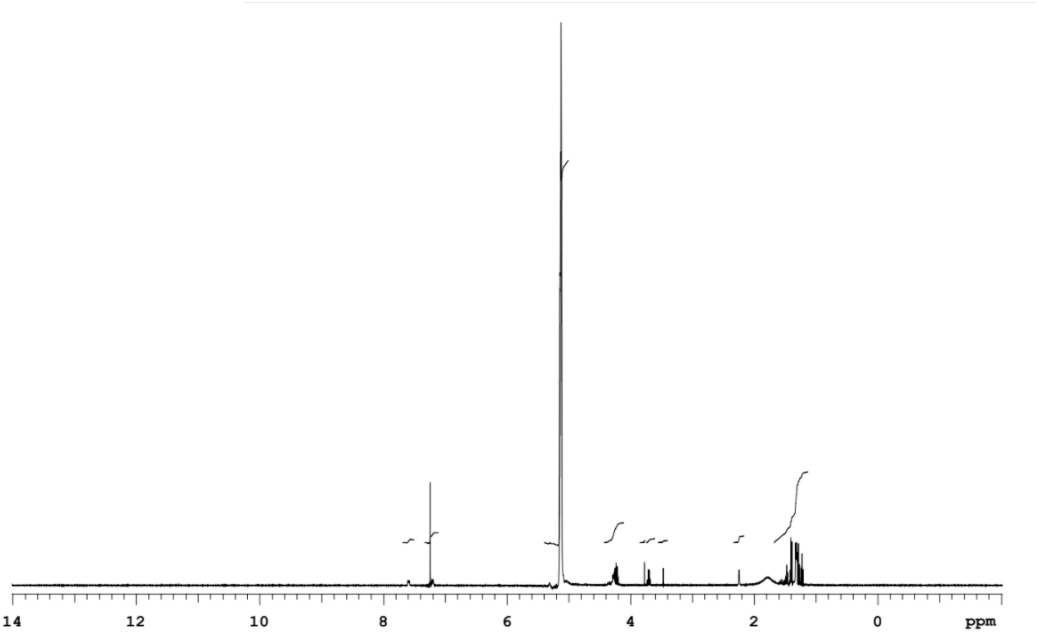


FIGURE B.1. ^{1}H NMR spectra of Synthesis of ethyl lactate, 10%.

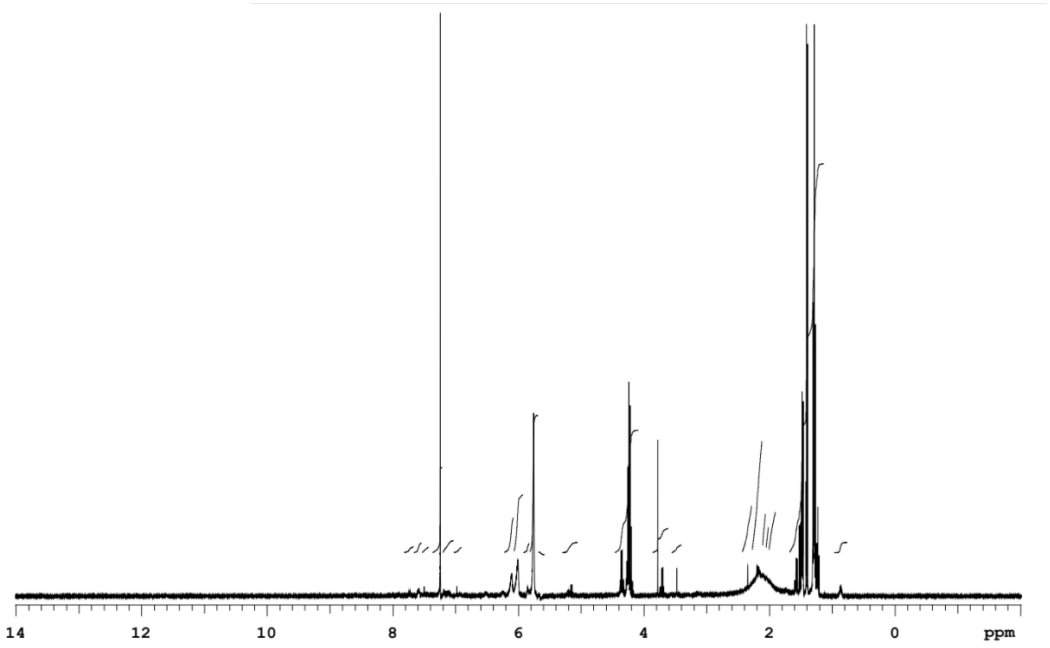


FIGURE B.2. ^{1}H NMR spectra of Synthesis of ethyl lactate, 20%.

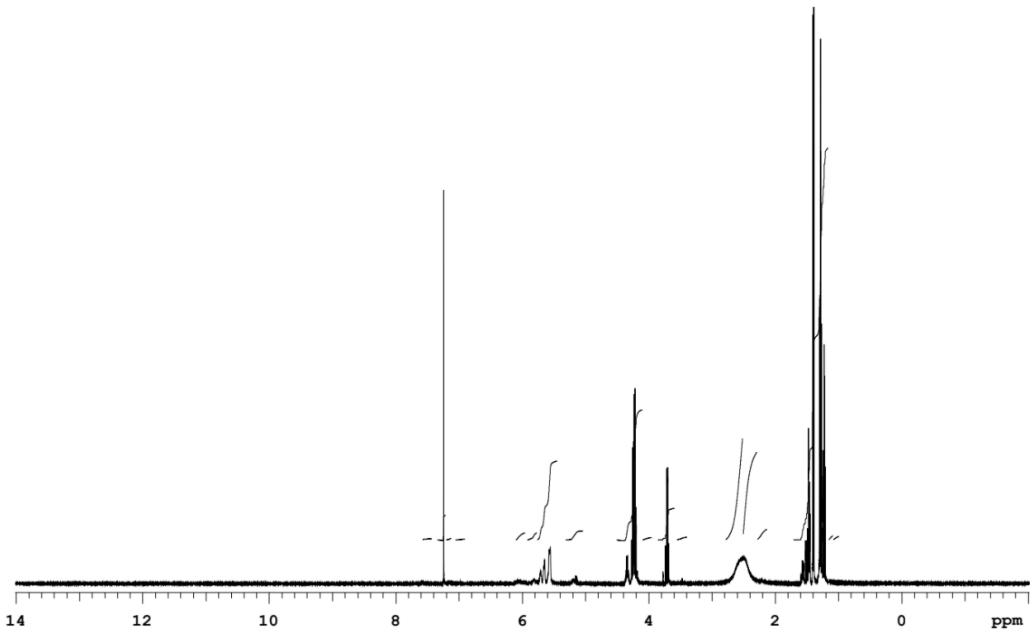


FIGURE B.3. ^{1}H NMR spectra of Synthesis of ethyl lactate, 50%.

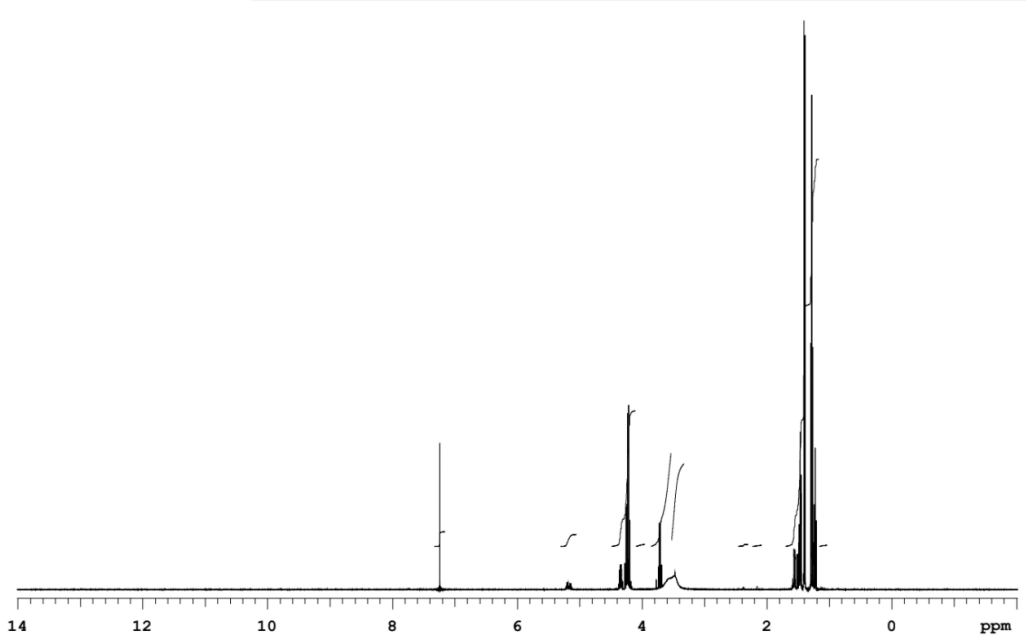


FIGURE B.4. ^{1}H NMR spectra of Synthesis of ethyl lactate, ~100%.

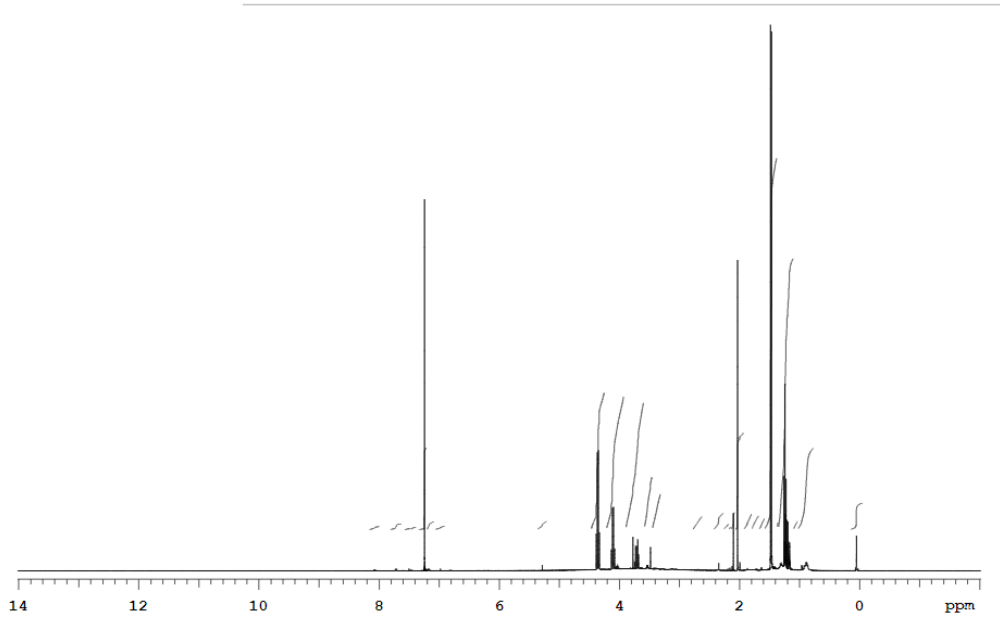


FIGURE B.5. ^{1}H NMR spectra *Direct conversion of ethyl lactate using* LA_{W20}, 1

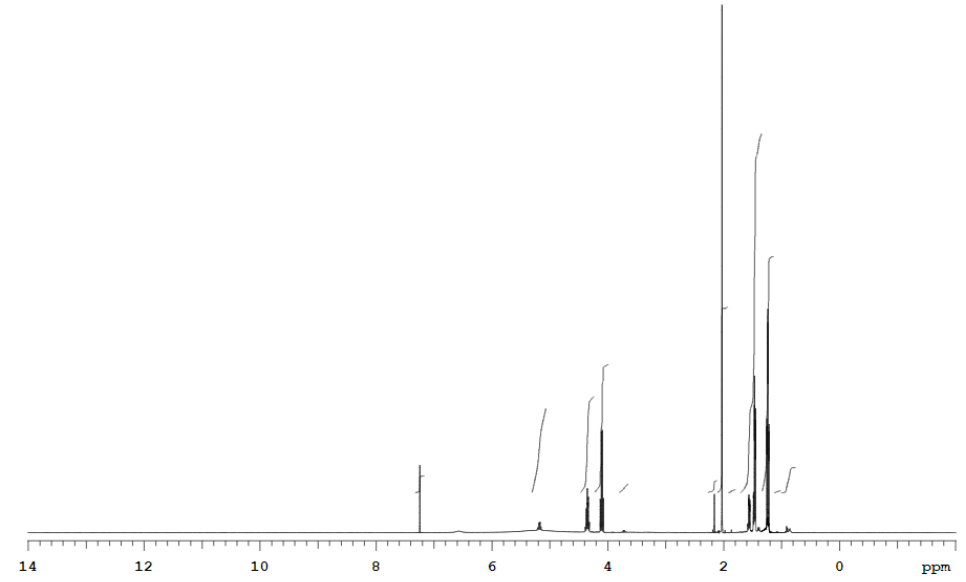


FIGURE B.6 ^{1}H NMR spectra *Direct conversion of ethyl lactate using* LA_{W20}, 2

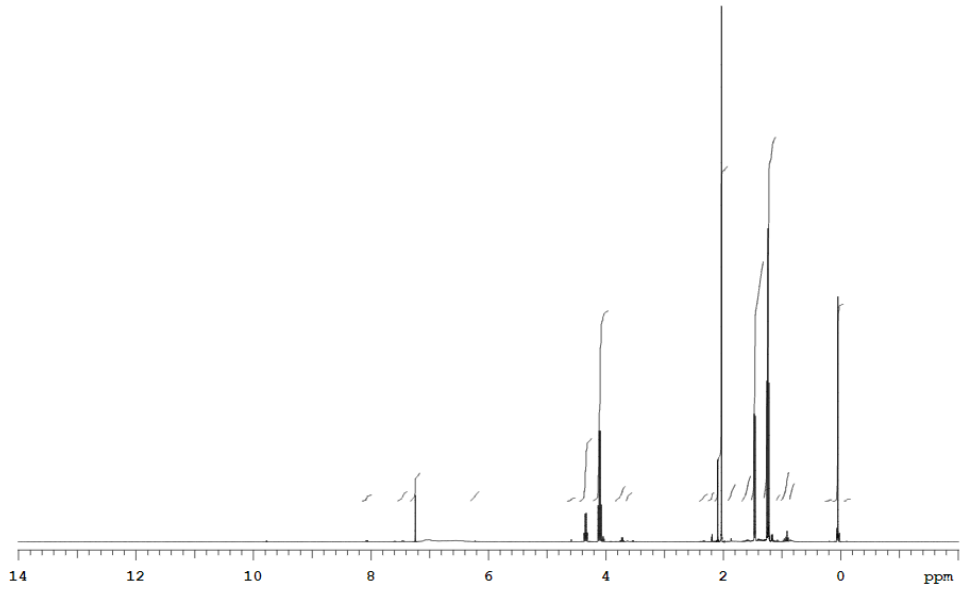


FIGURE B.7 1H NMR spectra Direct conversion of ethyl lactate using LA_{W20}, 3

Appendix C: ^{1}H NMR spectras - Synthesis of lactide

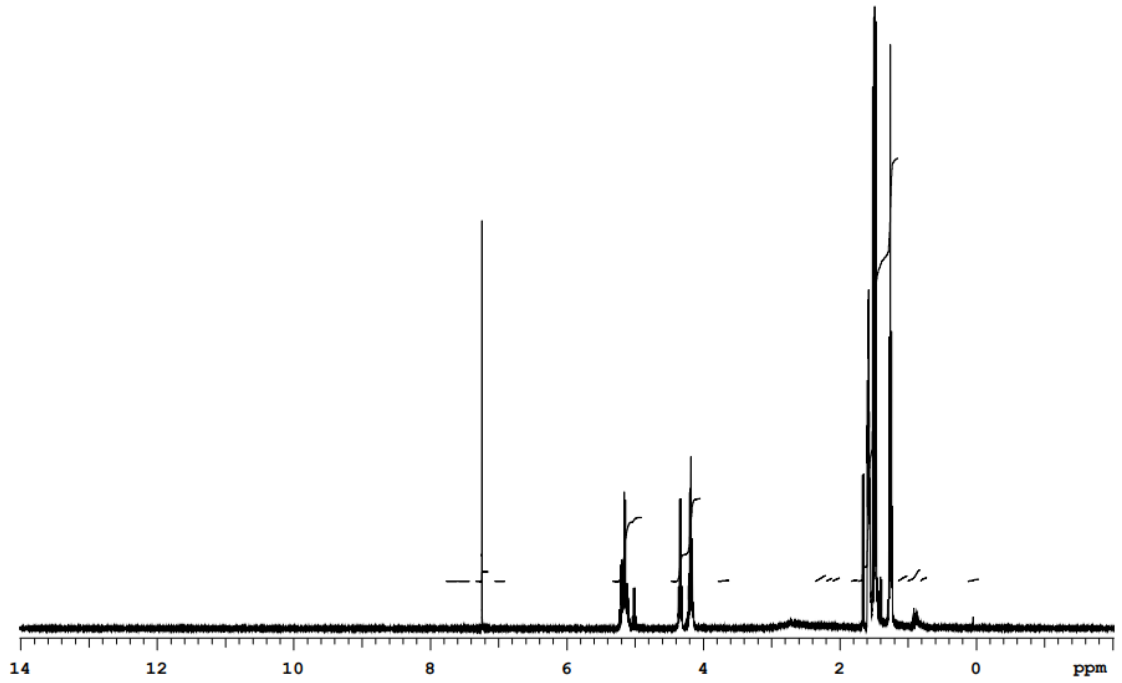


FIGURE C.1. ^{1}H NMR spectra of Synthesis of lactide (1) in Table 5.

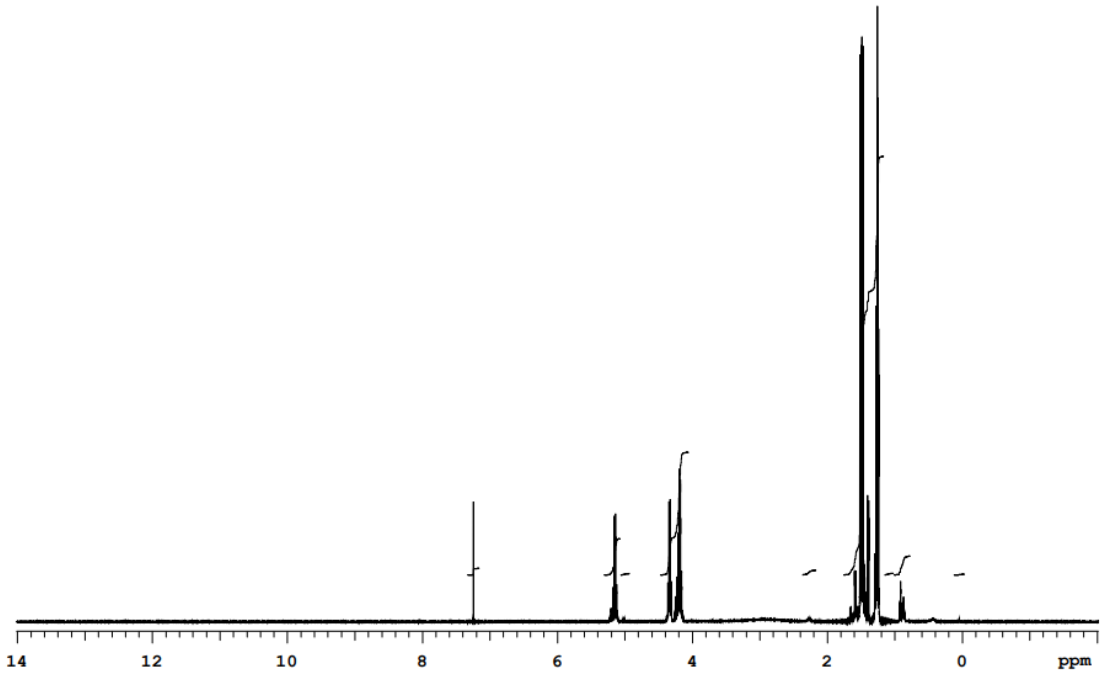


FIGURE C.2. ^{1}H NMR spectra of Synthesis of lactide (2) in Table 5.

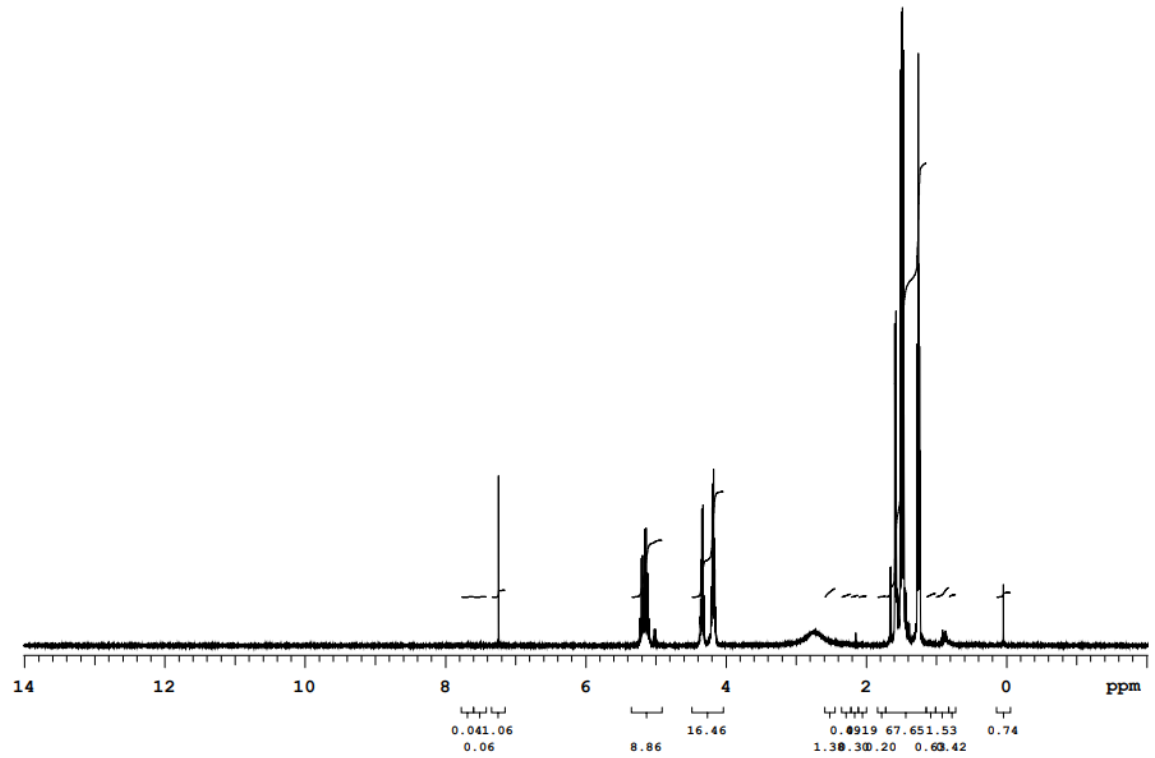


FIGURE C.3. ^{1}H NMR spectra of Synthesis of lactide (3) in Table 5.

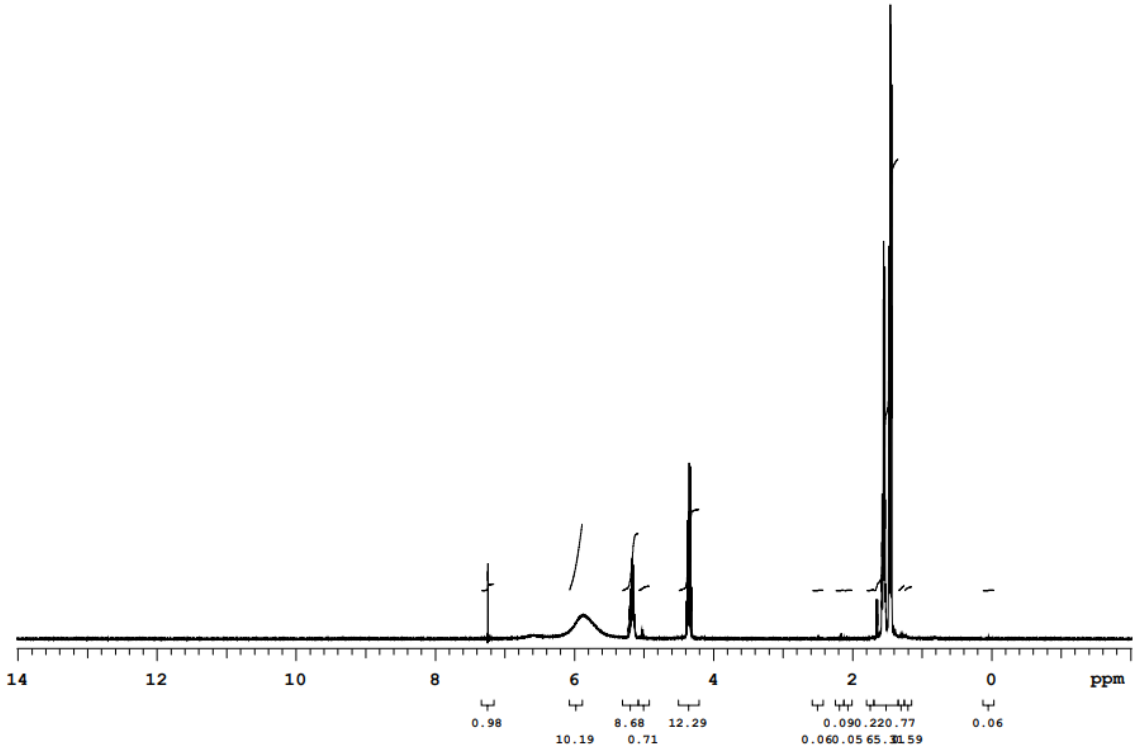


FIGURE C.4. ^{1}H NMR spectra of Synthesis of lactide (4) in Table 5.

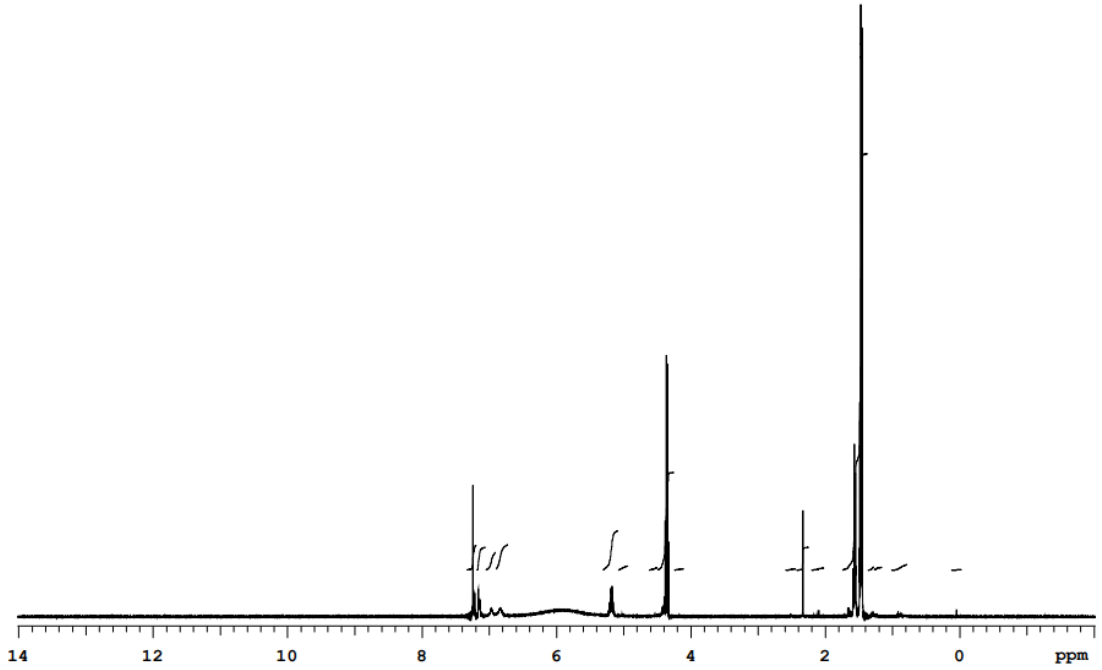


FIGURE C.5. ^{1}H NMR spectra of Synthesis of lactide (5) in Table 5.

Appendix D: ^{1}H NMR spectras - Microwave assisted synthesis of PLA

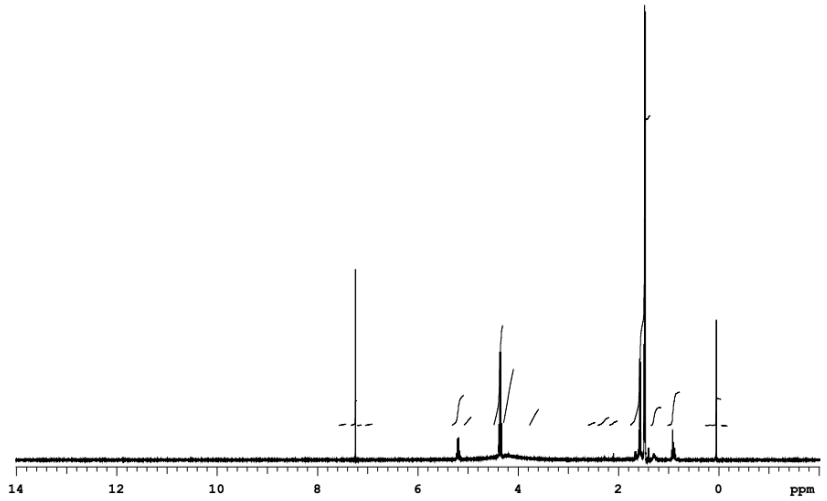


FIGURE D.1. ^{1}H NMR spectra of microwave assisted synthesis of PLA at 180°C using LA

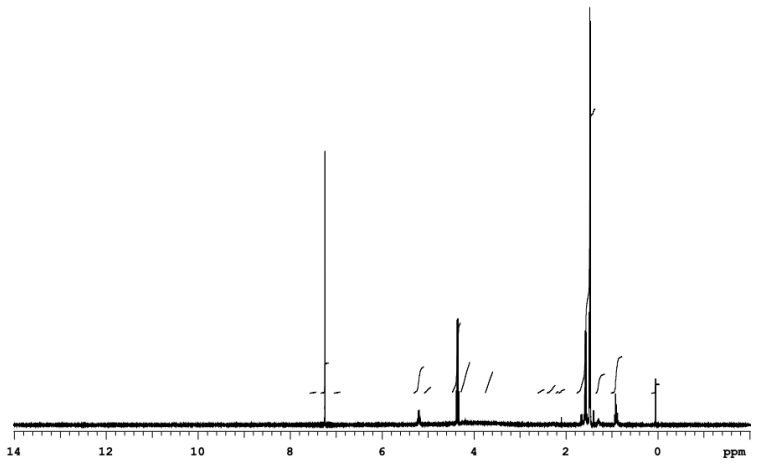


FIGURE D.2. ^{1}H NMR spectra of microwave assisted synthesis of PLA at 200°C using LA

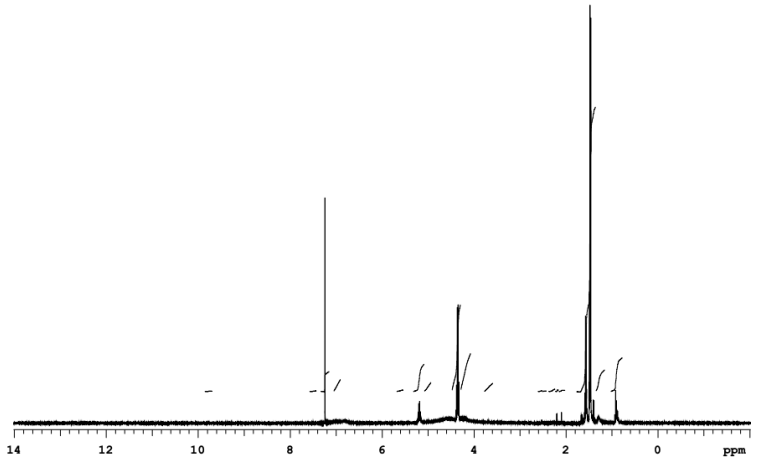


FIGURE D.3. ^{1}H NMR spectra of microwave assisted synthesis of PLA at 220°C using LA

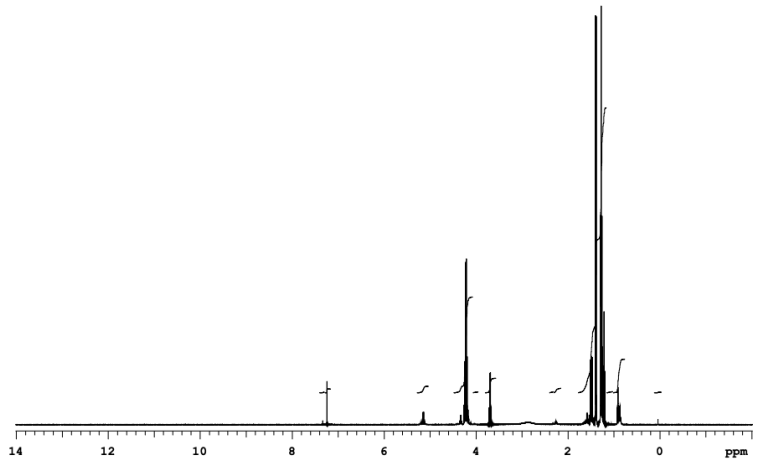


FIGURE D.4. ^{1}H NMR spectra of microwave assisted synthesis of PLA at 170°C using EtLA

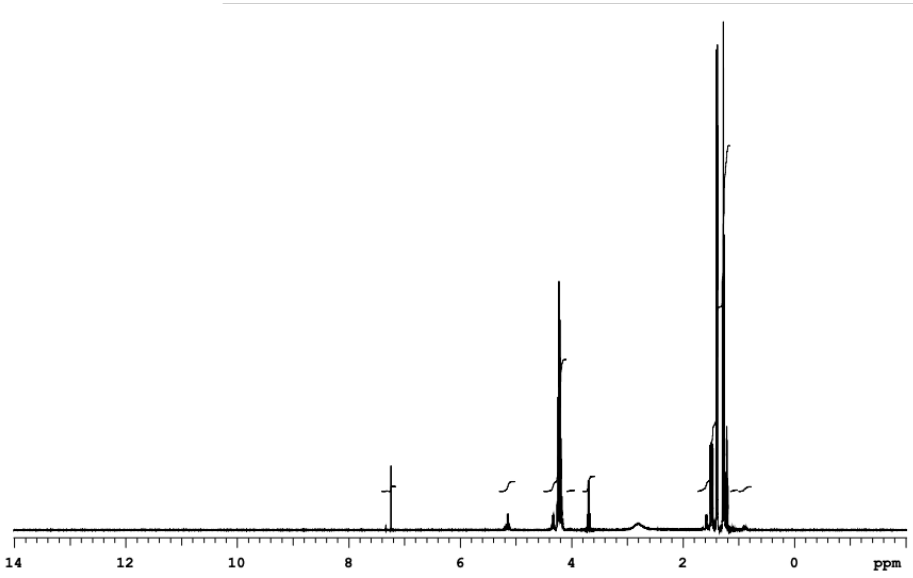


FIGURE D.5. ^{1}H NMR spectra of microwave assisted synthesis of PLA at 190°C using EtLA

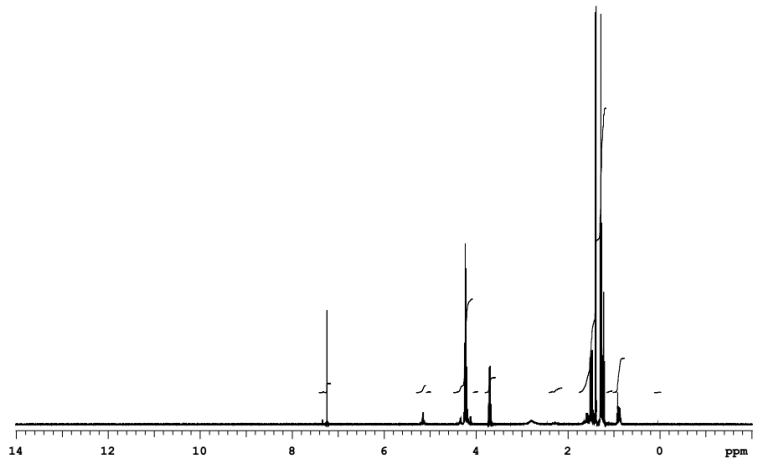


FIGURE D.6. ^{1}H NMR spectra of microwave assisted synthesis of PLA at 210°C using EtLA