**Methyl Lactate Production from the Degradation of Polylactic Acid By a Zinc Complex.**

Luis A. Román-Ramírez1, Paul McKeown2, Matthew D. Jones2 and Joseph Wood1,\*

*1 School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom.*

*2 Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom.*

*\*Corresponding author: j.wood@bham.ac.uk*

**Highlights**

* Oxygen stable Zn(II) complex used for the depolymerization.
* Main operating parameters identified through design of experiments.
* Reaction mechanism and kinetic modelling presented.
* Membrane separation process for product purification.

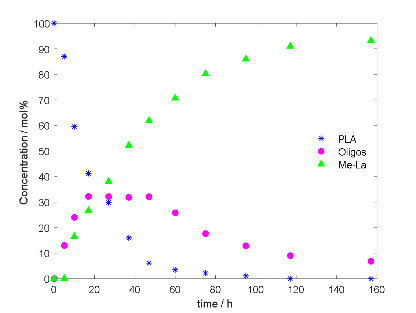
**1. Introduction**

Biodegradable-biorenewable polymers such as polylactic acid (PLA) are suitable candidates to replace synthetic oil-derived polymers. However, PLA can be still a potential source of environmental pollution. Chemical recycling presents an alternative to mechanical recycling or composting for end-of-life PLA that not only results in value-added products but that could also reduce production costs [1]. Although chemical recycling methods have been demonstrated in the literature (hydrolysis, acid-base depolymerization and transesterification) [2, 3], these processes are characterized for high temperatures (up to 260 °C). Milder operating conditions can be achieved in the transesterification reaction by using a complex metal catalyst. In this project, a Zn(**1**)2 complex was used for the PLA degradation to produce methyl lactate (Me-La). Main operating parameters for the process were studied by a design of experiments. A preliminary evaluation of the use of membranes and distillation for the purification step is also presented.

**2. Methods**

Small Initial trials of the PLA degradation were performed in a Schlenk flask, with 0.25 g of PLA and 22.4 mg catalyst at 50 °C. THF was selected as the solvent whereas methanol as the reactant. Zn(**1**)2 was first tested for oxygen stability. Me-La production was traced by GC and 1H NMR. Polymer disappearance was confirmed by GPC. With the aim to show scalability of the process, reactions were then performed in a 300 mL SS-316 stirred batch reactor. Operating parameters for the Taguchi design of experiments were: polymer concentration, polymer molecular weight, catalyst concentration and reaction temperature. Additionally, mass transfer limitations of the process were studied by including polymer particle size and stirring speed. The effects studied were: PLA conversion, Me-La selectivity, Me-La yield and maximum amount of Me-La produced. Sensible values of the range of operating parameters were included in the model. The effects were statistically analyzed. The progress of all the reactions was traced by withdrawing samples at different time intervals. Membrane separation studies were performed in a cross-flow system with a commercial membrane (Duramem 150), by varying pressure and temperature. Samples of the permeate were analyzed by GC and 1H NMR.

**3. Results and discussion**

Zn(**1**)2 was shown to be oxygen stable and easy to produce in large quantities. The statistical analysis of the results revealed that the main factors affecting conversion, selectivity and yield are temperature and catalyst concentration. No mass transfer limitations of the process were found. The maximum amount of Me-La produced only depends on the initial concentration of PLA. The observed experimental data was characteristic of two consecutive reactions showing formation of an intermediate and with the second reaction being reversible (Figure 1). The corresponding set of differential equations for the mass balance and rate equations were solved numerically coupled with a fitting procedure to get the kinetic constants for the different conditions studied. The temperature dependency of the kinetic constants for the PLA degradation step was evaluated by an Arrhenius type form. The activation energies obtained were in the range: 39 – 65 kJ/mol-1, which are of the order of magnitude of other PLA degradation processes that require higher temperatures. Preliminary separation studies show the possibility of removing intermediate products by a commercial membrane. Solvent and alcohol can be recovered by distillation.

**Figure 1.** PLA degradation experimental data.

**4. Conclusions**

Complete degradation of PLA was demonstrated by the use of a metal complex catalyst which is stable in the presence of oxygen and that can be easily scalable. A valuable chemical (methyl lactate) was produced from this degradation. The main operating parameters of the process were identified and a kinetic model proposed. Kinetic constants and activation energies were calculated from the model that can be used for reactor design and optimization.

**References**

1. Hong, M. and E.Y.X. Chen, *Chemically recyclable polymers: a circular economy approach to sustainability.* Green Chemistry, 2017. **19**(16): p. 3692-3706.

2. Petrus, R., D. Bykowski, and P. Sobota, *Solvothermal Alcoholysis Routes for Recycling Polylactide Waste as Lactic Acid Esters.* ACS Catalysis, 2016. **6**(8): p. 5222-5235.

3. Piemonte, V. and F. Gironi, *Kinetics of Hydrolytic Degradation of PLA.* Journal of Polymers and the Environment, 2013. **21**(2): p. 313-318.