

MODELING AND SIMULATION OF POLYMERIZATION OF LACTIDE TO POLYLACTIC ACID AND CO-POLYMERS OF POLYLACTIC ACID USING HIGH VISCOSITY KNEADER REACTORS

Boyd T. Safrit, LIST USA, Inc., Charlotte, NC

George E. Schlager, LIST USA, Inc., Charlotte, NC

Ziang Li, University of Texas at Austin, Austin, TX

Abstract

Polymerization of lactide to polylactic acid (PLA) can be performed using conventional reactor technology such as stirred tank reactors, but the conversion and/or final molecular weight may have to be controlled to a lower level. At higher conversion and/or molecular weight, the reaction mass will become very viscous, which limits the ability of conventional reactor technology to provide adequate mixing, minimize mass transfer effects on reaction kinetics, remove exothermic heat of reaction and ensure proper heat transfer in order to eliminate hotspots/thermal degradation.

Kneader reactor technology has been used over 60 years in many high viscosity applications such as reactions and polymerization, devolatilization, and drying. This technology can handle the higher conversion and molecular weight polymerizations of lactide and other copolymers of lactide, while also providing the heat transfer required for proper temperature control. Using model kinetics and rheology data, a study was performed that shows the capability of kneader reactor technology for lactide polymerizations as well as other copolymers. Kneader reactor technology can also be used to remove the unconverted monomers from the polymer and expected results from the continuous operation of a polymerizer and finisher will be shown.

Introduction

Stirred tank reactors and other conventional reactor technologies have been successfully used for many years in the polymerization and copolymerization of a variety of monomers. It is quite common in such reactions that the viscosity of the reacting mass will raise with increasing polymer molecular weight and that they are exothermic. These two characteristics pose challenges for conventional reactor technology. Stirred tank reactors, for example, are limited in their ability to maintain a well agitated and mixed reacting mass at higher viscosities. Reaction rates may therefore be reduced by mass transfer and diffusional limitations.

Poor agitation in stirred tank reactors may also contribute to low flow velocities near the reactor wall, resulting in low film heat transfer coefficients (reacting mass to inner reactor wall). Since the exothermic heat of

reaction in stirred tank reactors is typically removed via contact heat transfer with the reactor wall, the product temperature may increase uncontrollably, resulting in a run-away reaction or degraded product [1].

Kneader reactor technology is well suited for higher viscosity processing, including exothermic polymerizations. Kneading and mixing of viscous materials is provided by the interaction of the static and/or dynamic elements mounted on the shaft(s). Kneader reactors provide a large amount of heat transfer area from the jacketed reactor casing and the shafts and elements on the shafts are also actively heated/cooled with heat transfer media. Many products have a tendency to wrap around the shaft(s) of processing equipment and may lose contact with the surface area on the reactor casing. But kneader reactor technology has the additional agitated surface area on the shaft and shaft elements that can continue to provide heat transfer capabilities [2].

The polymerization of lactic acid via the ring opening reaction of lactide has become an important and frequently studied process in the last several years. New applications for polylactic acid (PLA) appear every day with ever increasing physical properties requirements [13]. Many medical applications, for example, require a higher molecular weight polymer than typically used for standard packaging applications. The monomer, lactide, is a low viscosity liquid at typical reaction temperatures but as the reaction proceeds and molecular weight increases, the viscosity of the reaction mass also increases. A study was performed on the polymerization of PLA with an emphasis on heat and mass transfer limitations encountered at higher molecular weight polymerizations. Using previously published kinetic models, a simulation model with simultaneous kinetic, degradation, molecular weight, viscosity, mass transfer, and heat transfer effects was developed. This model was used to simulate and compare the performance of a stirred tank (STR) and a batch kneader reactor. The same model was also capable of fully simulating continuous versions of these two reactor types.

Experimental

Kinetics

Witske (1996) developed a reversible kinetic model for the polymerization of lactide, catalyzed by tin octoate

in bulk. Equations 1-3 show the general model used in this study:

$$M(t) = M_{eq} + (M_0 - M_{eq})e^{-K_p t} \quad (1)$$

$$K_p = A e^{\left(-\frac{E_a}{RT}\right)} \quad (2)$$

$$M_{eq} = e^{\left(\frac{\Delta H_p}{RT} - \frac{\Delta S_p}{R}\right)} \quad (3)$$

Taking the derivative of Equation 1 and rearranging gives the basic dynamic kinetic model used in this study:

$$\frac{dM(t)}{dt} = K_p I (M - M_{eq}) \quad (4)$$

The effect of initiators was not included in this model. Mantourlias et al. (2008) investigated the effect of hydroxyl-containing initiator (R-OH) concentration and reaction temperature on yield. Vos et al. (2009) also show that the polymerization of lactide in the presence of an R-OH initiator is much faster than without the use of an initiator. It was assumed for our model that the presence of R-OH had an effect on the activation energy, E_a , only. Using the data of Mantourlias et al. (2008), we found that the effect of different R-OH initiators was small on the activation energy. However, the data of Vos et al. (2009) show that the pre-exponential constant may be affected by the choice of R-OH initiator. For our model, we used the Vos et al data to determine the pre-exponential constant and the Mantourlias et al data to determine the activation energy.

Viscosity

In order to model the reaction mass viscosity, the effects of monomer content, molecular weight, temperature, and shear rate had to be investigated. Dorgan et al. (2004) investigated the melt flow properties of PLA, including developing a zero-shear viscosity model based on the Carreau-Yasuda model. Using PLA zero-shear viscosity measurements taken at 180°C, Dorgan et al. proposed the following zero-shear viscosity model:

$$\eta_0 = 10^B M_w \left[1 + \left(\frac{M_w}{M_c} \right)^{p-1} \right] \quad (5)$$

Conrad (2009) measured PLA viscosity over a wide range of shear rates at 180°C and fit the data to the following power law viscosity model:

$$\eta_{PLA,pure} = \eta_0 \gamma'^{n-1} \quad (6)$$

Equation 7 is a common mixture viscosity model and was used to model the mixture of monomer (lactide) and PLA:

$$\eta_{mix} = \eta_{mon} + \frac{\eta_{PLA,pure} - \eta_{mon}}{1 + e^{\frac{x_0 - x}{w}}} \quad (7)$$

The data of Vos et al was used to get the best fit of equation 7, resulting in values of $x_0=70\%$ and $w=6\%$.

Molecular Weight and Degradation

Aoyagi et al. (2002) modeled the thermal decomposition of PLA using a linear relationship between the degree of polymerization (DP) and time, which is shown in Equation 8:

$$\frac{1}{DP} = \frac{1}{DP_0} + K_d t \quad (8)$$

$$K_d = \frac{3 * 10^{-9}}{hr} e^{\left(-\frac{103,000 \frac{J}{mol}}{RT}\right)} \quad (9)$$

We assumed for this study that the change in molecular weight during the polymerization was linear in the concentration change with time. Using this assumption of molecular weight change, the definition of DP, and Equation 8, the change in PLA molecular weight as a function of time due to degradation was:

$$\frac{dM_w(t)}{dt} = -K_d M W_{mon} \quad (10)$$

Equation 10 was combined with Equation 4 to give the overall dynamic kinetic polymerization model.

Mass Transfer

During most polymerizations, the reaction mass viscosity increases. At higher viscosities, most chemical reactors run into mass transfer limitations as these reactors are unable to provide adequate mixing of the viscous material and therefore the reaction kinetics become negatively impacted. At these higher viscosities, the effective reaction rate approaches the diffusional mass transfer rate. We assumed a resistance based model for mass transfer in order to estimate an effective kinetic rate constant, K_{eff} :

$$\frac{1}{K_{eff}} = \frac{1}{K_p} + \frac{1}{K_{diff}} \quad (11)$$

K_{eff} would replace K_p in Equation 1. In order to estimate the diffusional mass transfer coefficient, K_{diff} , we assumed as many models do (e.g. Stokes-Einstein and Wilke-Chang models) that the mass transfer coefficient was inversely proportional to the reaction mass viscosity. Using the data from [5] at 50ppm catalyst concentration, we fit a correlation for the mass transfer coefficient:

$$K_{diff} = \frac{250Pa \cdot s \cdot hr^{-1}}{\eta_{mix}} \quad (12)$$

This data was chosen in order to minimize any temperature effects due to heat transfer limitations that may occur at higher catalyst loadings. While mass transfer coefficients are largely dependant on the processing equipment in use, in this study we assumed that the mass transfer coefficient was the same for all reactor types.

Heat Transfer

For the same reasons mass transfer can be an issue in polymerizations, heat transfer must also be included. In a STR for example, as the reaction mass viscosity increases, the ability to maintain a well mixed reactor goes down, which reduces the heat transfer rate at the walls of the reactor. Localized hot spots may develop in the reaction mass, leading to degradation and possible run away reactions.

It was assumed that the flow regimes within either the modeled STR or kneader reactor was in the laminar range. We used the following heat transfer coefficient correlation, developed for agitated vessels, for the inside reactor wall [9]:

$$h_{inside} = \frac{k}{D} a (N_{Re})^b (N_{Pr})^{\frac{1}{3}} \left(\frac{\eta_{bulk}}{\eta_{wall}} \right)^m \quad (13)$$

N_{Re} and N_{Pr} were calculated in the typical manner for the STR. For the kneader reactor, proprietary calculations were used for these parameters. The heat transfer area for the STR was assumed to be the entire wall of the reactor. Kneader reactor technology is never operated 100% full and is normally operated with a fill level of 50-70%. The heat transfer area assumed for the kneader reactor was the total internal heat transfer surface area of the kneader reactor scaled by the assumed fill level.

Results and Discussion

All model characteristics previously detailed were incorporated into a dynamic model so that both batch and continuous reactors could be simulated. The results of a batch stirred tank reactor and a batch kneader reactor follow. We assumed the data of [5] was taken on a small, laboratory stirred flask of 1 liter with a constant heat bath temperature of 180°C.

Small Batch Stirred Tank Reactor

Figure 1-A shows the experimental conversion data of [5] and the results of the simulation model (no mass transfer or temperature effects). Figure 1-B shows the same data but rearranging Equation 1 so that the kinetic model would form a straight line when plotted against time. All results assume a constant reaction temperature of 180°C. The data and model agree well for the case of 50ppm catalyst loading. In this case, the polymerization

proceeded slowly, which most likely allowed the experimental reactor (assumed to be a small laboratory stirred flask) of [5] to maintain a constant reaction temperature of 180°C. After a polymerization time of 3 hours, there is a deviation in the data and model. We believe that at this point the reaction mass viscosity has increased so that mass transfer limitations in the experimental reactor are negatively impacting the reaction rate, especially at higher conversions (viscosity). At higher catalyst loadings, we see conversions higher than expected during the early part of the polymerization. It is possible that the experimental reactor could not remove the exothermic heat of reaction fast enough due to the higher rate of reactions. In this case, the reaction mass temperature would increase and the reaction rate would therefore increase. Figure 2-A shows the conversion results of the model when temperature and mass transfer effects were included. For the 50ppm case, the conversions are over-predicted, however, for higher catalyst loadings, the conversions are under-predicted. Figure 2-B shows the predicted temperature profiles for several of the different catalyst loadings. The shape and maximal value of the temperature profiles was very sensitive to the heat transfer coefficient calculation. The data of [5] did not include any temperature information so determining better heat transfer coefficients was not possible. One other interesting outcome shown on Figure 2-B was the saddle in the temperature profile. The reaction mass was assumed to be at 180°C at $t=0$ and the heat transfer medium was also assumed to be 180°C. When the reaction started, the rate of heat transfer is very low due to a small temperature difference. There was a lag between the heat transfer out of the system and the heat added to the system via the exothermic heat of reaction. The influence of increasing mixture viscosity on the heat transfer coefficient also contributed to the saddle in the temperature profile.

Small Batch Kneader Reactor

A simulation of a batch kneader reactor was carried out and the size of the reactor was chosen so that the mass of polymer (~1.2 kg) was the same as the small batch STR. As can be seen in Figure 3 (A&B), the results of the kneader reactor are similar to the batch STR. The maximum temperature for each catalyst loading was less in the kneader reactor than the STR due to the fact that the surface to volume ratio of the kneader reactor was approximately $74m^2/m^3$ compared to the STR of 46. The heat transfer coefficients were also higher in the kneader reactor since the kneader reactor operates at a higher shear rate than the STR. The effect of shear rate on mass transfer limitations was also very important at higher viscosities and PLA molecular weights as the kneader reactor was not affected as much as the STR.

Commercial Scale

The model was used to simulate a commercial PLA continuous polymerization process of 10,000 ton/year using a catalyst concentration of 100ppm. The targeted conversion of lactide to PLA was 95% with a molecular weight of 150,000 g/mol. A heat transfer medium temperature of 180°C was also assumed. The results of the continuous stirred tank reactor (CSTR) can be seen in Table 1. The same process assumptions were used for the continuous kneader reactor model and are shown in Table 1. The CSTR reactor volume and the kneader reactor volume were chosen to allow the reaction to reach the specified conversion. It is interesting to note that the CSTR required to complete the specified reaction was 125,000 liters, while the required kneader size is only 2,900 liters. Figure 4 shows the temperature profile for the kneader reactor as a function of axial position in the reactor. The maximum temperature is 194°C, which is similar to the CSTR. However, the polymer would be at this temperature for only a fraction of the total 1.7 hr residence time in the kneader reactor. The polymer in the CSTR would be subjected to 195°C for the entire residence time of 3.8 hrs. Thermal degradation reactions are a function of both time and temperature, meaning the CSTR would be much more susceptible to polymer degradation.

Table 1: Commercial Reactor Model Results

		CSTR	Kneader
Volume	L	125,000	2,900
Surface area	m ²	117	43
Reactor temperature	°C	195	194 (max)
Reactor viscosity	Pa*s	300	18 (max)
Residence time	hr	3.8	1.7

Table 1 also shows the viscosity for both the CSTR and the kneader reactor (maximum value.) The difference in the viscosities of the two reactor types is due to the shear rate dependency. The kneader reactor operated at a higher shear rate, which lowered the effective reaction mass viscosity. At a viscosity of 300 Pa*s, the ability of CSTR technology to adequately maintain a well mixed environment will be limited. This could possibly lead to local hot spots, degraded polymer, etc. For higher target molecular weight products and possibly co-polymers of lactide and other monomers, high viscosity and heat/mass transfer limitations may require technology like kneader reactors that are more suited to high viscosity processing.

Most commercially available PLA has a specification of residual lactide of <0.5wt%. For the commercial polymerization process, a devolatilization step must be added in order to remove the residual monomer (lactide) down to an acceptable level. As pointed in [11] and [12], kneader reactor technology is also very suitable to the devolatilization of temperature sensitive polymers. Figure 5 shows a typical two-stage kneader reactor process for the polymerization and devolatilization and PLA. As shown in [12], lactide levels in the final PLA polymer

could be much lower than the typical commercial specifications of < 0.5wt%.

Conclusions

A model was developed for the polymerization of lactide to polylactic acid. This model included the effects of kinetics, heat and mass transfer, viscosity, molecular weight, and reactor technology (stirred tank reactors and kneader reactors.) Lactide conversion data of [5] showed that as catalyst concentration was increased, heat and mass transfer limitations of the lab reactor negatively impacted the polymerization process. A kneader reactor was simulated and these limitations were minimized.

A commercial scale continuous process was also simulated. A continuous stirred tank reactor required for this throughput was very large and resulted in a higher product temperature over the entire residence time, which could lead to high polymer thermal degradation. The required kneader reactor however was much smaller in size and minimized the heat history of the polymer. The commercial kneader reactor polymerizer could also be matched with a kneader reactor devolatilizer for removing the residual monomer (lactide.)

Nomenclature

a	heat transfer correlation coefficient = 0.36 for STR and 0.74 for kneader reactor
b	heat transfer correlation coefficient = 2/3
A	pre-exponential constant
B	zero shear rate constant = -4.87
D	reactor diameter
DP	degree of polymerization
DP ₀	initial degree of polymerization at t=0
E _a	activation energy = 76,830 J/mol
ΔH _p	enthalpy of polymerization = -23,300 J/mol
h _{inside}	reactor wall heat transfer coefficient
I	catalyst concentration in mol%
k	reaction mass thermal conductivity = 0.289 W/m-K
K _{eff}	effective kinetic rate constant
K _{diff}	diffusion rate constant
K _p	propagation rate constant in catalyst mol% ⁻¹ hr ⁻¹
K _d	degradation reaction rate constant
m	heat transfer correlation coefficient = 0.21
M _w	polymer molecular weight
MW _{mon}	monomer molecular weight = 144.13 g/mol
M(t)	monomer concentration at time (t)
M _{eq}	equilibrium monomer concentration
M ₀	initial monomer concentration
M _w	polymer molecular weight in kg/kg-mole
M _c	critical entanglement molecular weight = 9211 kg/kg-mole
n	power law index = 0.23 for PLA
N _{Re}	Reynolds number
N _{Pr}	Prandtl number
p	chain packing length = 3.5

ΔS_p	entropy of polymerization = -22 J/mol-K
T	temperature
x	weight fraction of PLA in the mixture
x_o	cross over weight fraction = 0.7
w	band width weight fraction = 0.06
γ	apparent shear rate in sec^{-1}
η_0	zero shear viscosity in Pa*sec
$\eta_{\text{PLA,pure}}$	pure PLA viscosity at the apparent shear rate
η_{mon}	monomer viscosity
η_{mix}	mixture viscosity
η_{bulk}	reaction mass bulk viscosity
η_{wall}	reaction mass viscosity at reactor wall

- M. H. Naitove, "Conference Report: Bioplastics Are Breaking Out of Their 'Green' Niche", *Plastics Technology* (April 2012).

Key Words

kneader reactor, polymerization, devolatilization, high viscosity, heat transfer, PLA, lactide, polylactic acid, bulk polymerization, mass transfer.

References

- P. A. Fleury, "Bulk Polymerization of Methyl Methacrylate in a Kneader Reactor", Presented at ANTEC 2006 (2006).
- B. T. Safrit, "Prediction of Continuous Kneader Reactor Processes From Batch Data", ANTEC 2007 Technical Paper # ANTEC-0425-2007 (2007).
- D. Witzke, "Properties and Engineering of Polylactide Polymers", Thesis, Michigan State University (1996).
- T. Mantourlias, A. Seretis, K. Karidi, S. Parouti, C. Kiparissides, "Lactic Acid Based Functional Copolymers", *Bioproducts 2nd Annual Meeting* (2008).
- S. de Vos, P. Jansen, "Industrial-Scale PLA Production from PURAC Lactides", 8th World Congress of Chemical Engineering (2009).
- J. Dorgan, D. Knauss, J. Janzen, J. Randal, B. Braun, O. Gruber "Perfecting PLA Properties: A Successful University Collaboration", *The Global Plastics Environmental Conference* (2004).
- NatureWorks® PLA Injection Molding Guide for 3051D.
- J. Conrad, "The Rheology, Degradation, Processing, and Characterization of Renewable Resource Polymer's", Thesis, Clemson University (2009).
- C. Geankoplis, *Transport Processes and Unit Operations* (1983).
- Y. Aoyagi, K. Yamashita, and Y. Doi, "Thermal degradation of poly[(R)-3-hydroxybutyrate], poly[ϵ -caprolactone], and poly[(S)-lactide]", *Polymer Degradation and Stability*, Vol 76, pp 53-59 (2002).
- P. A. Fleury, D. U. Witte, H. Schildknecht, "Comparison of Devolatilization Technologies for Viscous Polymers", ANTEC 2005 Technical Paper #100655 (2005).
- B. T. Safrit, A. E. Diener, "Kneader Technology for the Direct Devolatilization of Temperature Sensitive Elastomers", Rubber Division of the American Chemical Society, Inc. 180th Technical Meeting, Paper #13 (2011).

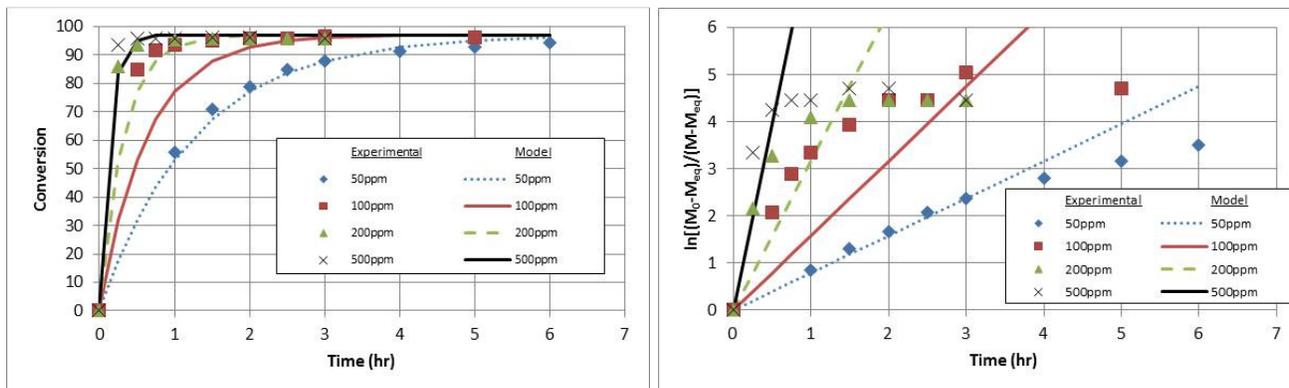


Figure 1 (A&B): Monomer Conversion (Experimental and Model) with No Temperature of Mass Transfer Effects

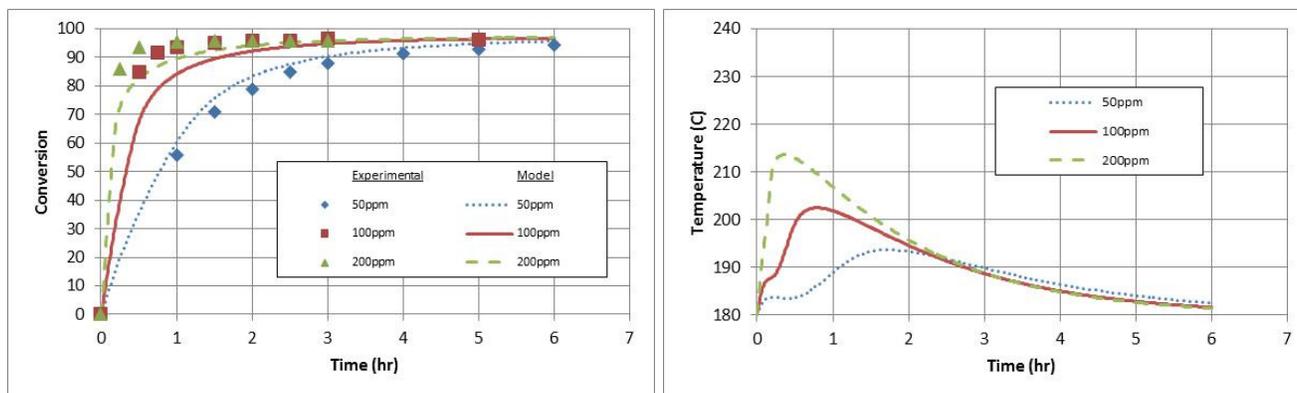


Figure 2 (A&B): STR Monomer Conversion (Experimental and Model) and Model Temperature Profiles with Temperature of Mass Transfer Effects

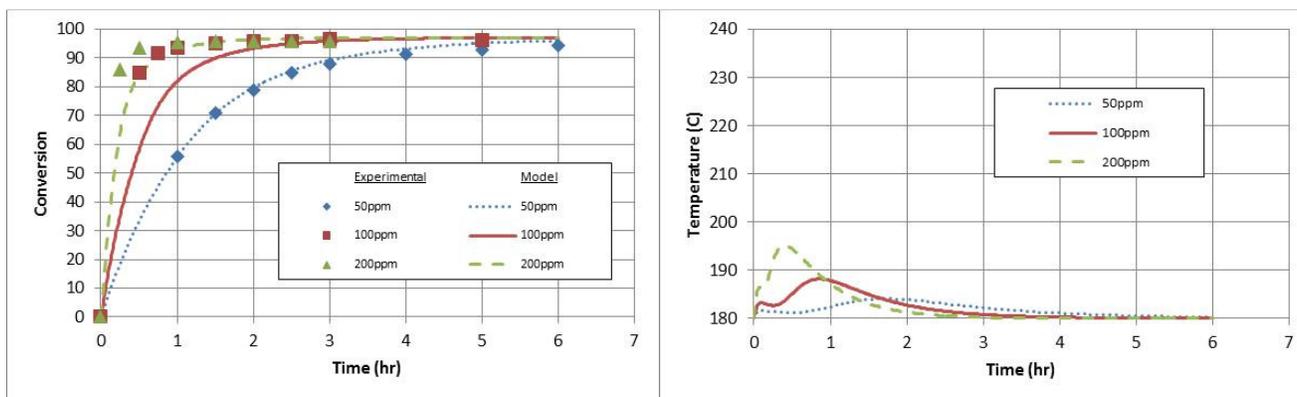


Figure 3 (A&B): Kneader Reactor Monomer Conversion (Experimental and Model) and Model Temperature Profiles with Temperature of Mass Transfer Effects

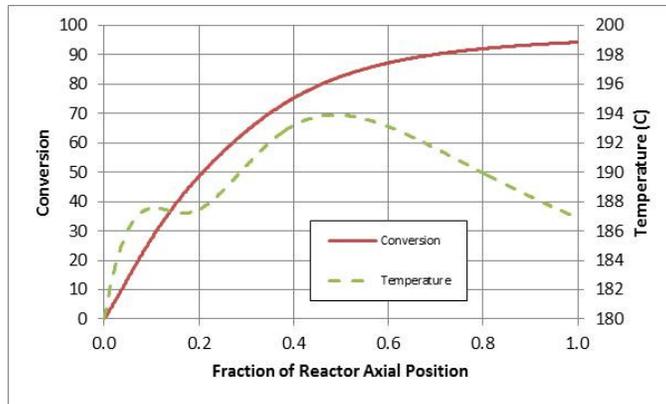


Figure 4: Model Results for Commercial Kneader Reactor

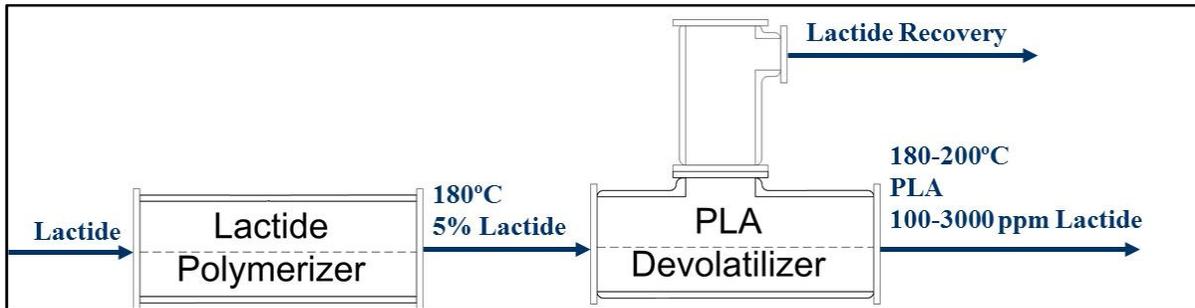


Figure 5: Two-Stage Kneader Reactor PLA Process