

# Prediction of Kneader Reactor Bulk Co-Polymerization Continuous Processes From Batch Data

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## Abstract

Batch trials were performed on a kneader reactor where a bulk co-polymerization was carried out. Polymerization conversion, viscosity build, reaction kinetics, and heat transfer calculations were performed using the experimental data from the batch trials. A continuous process was proposed for this bulk co-polymerization and the models and results from the batch trials were used in designing the continuous process. Predictions of the continuous process using the batch trial data are compared to the actual continuous process, with a focus on polymer conversion, heat transfer, and torque prediction.

## Introduction

Kneader reactor technology has been used over 30 years for a variety of applications including drying, polymer/rubber devolitization, solvent recovery from sludge, and liquid based reactions and polymerizations. In the case of bulk polymerizations, typically one or more liquid reactants are fed to the reactor with a catalyst or initiator. As the polymerization proceeds, the rheological behavior of the material in the reactor may change. The material may turn into a gel, become thicker and turn into a pasty phase. The material may eventually turn over into a solid and form granules or powder. If the reaction is exothermic, the heat of reaction may need to be removed to prevent thermal degradation, gel or Trommsdorff's effect, runaway reactions, or other undesired phenomenon (1).

A kneader reactor is well suited to carry out exothermic bulk polymerizations. Heat transfer area provided in the casing jacket, shaft, and shaft kneading elements can remove the exothermic heat of reaction and mechanical heat input in order to maintain the proper reaction temperature. Evaporative cooling can be utilized to remove this heat by evaporating/condensing/refluxing one or more of the reactants (1). In the absence of evaporative cooling however, heat transfer area must provide all of the heat transfer out of the polymer mass. Understanding the heat transfer is very important when the process is to be scaled up to larger capacities.

The kneading/cleaning elements of the kneader reactor provide constant surface renewal, which improves heat transfer by reducing stagnant zones of polymer that

may insulate against heat transfer. These elements also reduce or eliminate the diffusion and mass transfer limitations of the reaction by keeping the polymer mass well mixed radially (for a plug flow design reactor) or radially and axially (for a back-mixed design reactor.) Reaction residence times can be significantly reduced if the mass transfer limitations are minimized. The cleaning elements also continually wipe and clean the casing walls, shaft(s) and kneading elements, which reduces stagnant zones of polymer and thermal time-dependant degradation.

Bulk polymerizations are often characterized by high viscosity, which translates into high shaft torque. In a batch or back-mixed design reactor, the torque is evenly distributed along the shaft. In a plug flow or continuous reactor, the torque may not be distributed evenly. For example, processes that are characterized by material that turns over into a solid from a liquid or pasty phase can have a large torque increase over a small section of the shaft. The design of the kneader reactor shaft(s) and kneading/cleaning elements is crucial and must take into account the total torque requirement and the distribution of this torque.

An exothermic co-polymerization was carried out in a 12-liter batch kneader reactor. Polymer temperature, shaft torque, cooling medium inlet and outlet temperatures, and conversion were measured as a function of batch reaction time (residence time) for several batch trials. Reaction kinetics, shaft torque relationships, and heat transfer coefficients were determined from this data and a model for a continuous reactor was developed. Continuous trials were performed using a 31-liter reactor and the results from these trials were compared against the model predictions.

## Experimental

The batch trials were performed on a twin shaft, co-rotating 12-liter kneader reactor. The reactor had a jacket on the casing and actively cooled shafts that provided the necessary heat transfer area. A glycol/water mixture was circulated through the jacket and shafts as a heat transfer medium. The shafts were rotated by a hydraulic drive system that was manually adjusted in order to target the specific shaft RPM. For each trial, the reactor was flushed with the specific monomer mixture, drained, and then blanketed with a slight overpressure of nitrogen.

Monomer mixture was metered into the reactor to an approximate fill level of 60%. Catalyst was injected using a syringe directly into the reactor and the shafts were rotated at 20-30 RPM for a brief period in order to mix the monomer mixture and catalyst. Due to the shear sensitivity of the polymer, the shafts were rotated at a very low RPM for all of the batch trials. Samples were manually removed during each trial and tested for polymer conversion. Process data was continually collected during each trial using a data acquisition system, which included: coolant inlet and outlet temperatures on the shafts and casing, process chamber temperature, and oil pressure of the hydraulic drive system.

The continuous trials were performed on a twin shaft, co-rotating 31-liter kneader reactor that was equipped with a twin-screw discharge system. The rotation speed of the reactor shafts was higher than in the batch trials. Samples of the discharge from the twin-screw discharge system were tested for polymer conversion and the same process data was collected as in the batch trials.

## Results and Discussion

### Reaction Kinetics Scaleup

Figure 1 shows the relationship between conversion and batch residence time for three of the batch trials. The polymerization reaction proceeded quickly in the first 2-3 hours of reaction time but the rate of conversion diminishes in the later stages of the polymerization. The target conversion was 80%. A kinetic model based on the batch trial data, also shown in Figure 1, was developed in order to predict the polymerization conversion as a function of residence time (axial length) in the continuous kneader reactor.

A residence time of approximately 8 hours was targeted for the continuous kneader reactor using Equation 1:

$$t_r = \frac{V_r \phi_r \rho_p}{F_p} \quad (1)$$

Based on the kinetic model, the expected conversion should have been 70%. During a continuous period of roughly 24 hours in two separate continuous trials, conversions of approximately 80% were realized in the kneader reactor (see Figure 2 a and b). This result is in close agreement to the prediction of the batch kinetic model. Improved mixing and surface renewal due to a higher shaft rotational speed in the continuous trials could be one explanation of the improved kinetics.

### Torque Scaleup

The oil pressure of the hydraulic drive system was recorded as a function of reaction time during the batch trials and is shown in Figure 3. As the polymerization

proceeded, the viscosity of the polymer increased, thereby increasing the torque of the reactor shafts. Hydraulic pressure was converted to torque using Equation 2:

$$M_r = M_{spec} (P_{load} - P_{empty}) \quad (2)$$

where  $M_{spec}$  is the specific torque of the reactor/hydraulic drive combination and  $P_{empty}$  is the hydraulic pressure of the empty reactor (bearings, tightness of stuff box packings, etc. will affect  $P_{empty}$ ). The batch trials were broken into three sections of equal time and an average and maximum hydraulic pressure within each section was calculated (see Figure 3.) Table 1 shows the corresponding torque (shown in units Nm/liter by dividing torque by reactor volume) for each section on an average and maximum hydraulic pressure basis. Also shown is the distribution of the torque during the reaction time. For example in the case of the batch trial average date, 48% of the total torque (30 Nm/liter is the average of the three sections) was distributed on Section 3 (reaction time between 8 and 12 hours). If this profile was translated onto a continuous process, 48% of the total torque would be applied to the final 1/3 of the shaft length. For high overall torque applications where there may be a high concentration (distribution) of the torque on a small section of the shaft length, the design of the shaft and the kneading/cleaning elements must be carefully considered.

To scaleup the small batch reactor torque requirements to a larger continuous reactor, 30 Nm/liter was used as the basis. Figure 2 shows the hydraulic pressure for a period of time during continuous trials 1 and 2. The average and maximum hydraulic pressures for each trial are also shown and are included in Table 1. The average hydraulic pressure of 59 bar corresponds to 26 Nm/liter, which agrees with the prediction of 30Nm/liter.

### Heat Transfer Scaleup

Temperature data collected during the batch trials was used to generate a heat transfer model of this polymerization process. In particular, the temperature of the coolant medium and the process chamber (polymer) temperatures were used. Using Equations 3-6, the amount of heat that was removed from the reactor using the coolant was calculated. This heat was made up of the heat of reaction,  $Q_r$ , and the mechanical energy input,  $Q_{mech}$ , due to the rotation of the shafts. Using the known heat transfer area,  $A$ , and calculated temperature difference,  $\Delta T$ , an overall heat transfer coefficient,  $k$ , was calculated.

$$Q_r = F_p \Delta H_r X \quad (3)$$

$$Q_{mech} = M_r n \quad (4)$$

$$Q_{total} = Q_r + Q_{mech} = kA\Delta T \quad (5)$$

$$\Delta T = T_p - T_c \quad (6)$$

Figure 4 shows the variation of  $k$  as a function of batch residence time for batch trial #1. The heat of reaction and

mechanical energy components of the total energy removed are also shown. As the polymerization proceeded, the heat of reaction component decreased since the rate of reaction decreased. However, the mechanical energy increased due to the viscosity build of the polymer in the reactor. An overall heat transfer coefficient of approximately  $50 \text{ W}/(\text{m}^2\text{-K})$  was calculated with a  $\Delta T$  of roughly 3-4 K. With a small  $\Delta T$  such as this, any errors in the polymer temperature,  $T_p$ , or the coolant temperature,  $T_c$ , have a large effect on  $\Delta T$  and a corresponding large effect on the calculated heat transfer coefficient.

Due to the design of the particular kneader reactors used in the batch and continuous trials and the position of the temperature sensors in the reactors, the process chamber temperature was not a very accurate measure of the true polymer temperature. Actual polymer temperatures were taken during the continuous trials using a handheld temperature sensor. Measurements were taken at the beginning, middle, and end of the reactor at the polymer surface and polymer bulk closer to the shaft. A log mean  $\Delta T$  was calculated for each section using the measured actual polymer temperatures and recorded coolant temperatures. For continuous trial 1, the average log mean  $\Delta T$  was 2.8K. Mechanical energy input was calculated using Equations 2 and 4 and the heat of reaction energy input was calculated using Equation 3 at  $X=80\%$ . Equation 5 resulted in an average overall heat transfer coefficient of  $229 \text{ W}/(\text{m}^2\text{-K})$ , which did not compare well with the prediction from the batch trials of  $50 \text{ W}/(\text{m}^2\text{-K})$ . If the process chamber temperature measurement is used in the  $\Delta T$  calculation instead of the actual polymer temperature,  $\Delta T= 9.5\text{K}$  and the effective overall heat transfer coefficient would be  $68 \text{ W}/(\text{m}^2\text{-K})$ , which is much closer to the batch trial prediction.

## Conclusions

A 12-liter twin-shaft batch kneader reactor was used to carry out an exothermic bulk polymerization. Process data was measured and polymer samples were analyzed for conversion so that models of polymerization kinetics, shaft torque, and overall heat transfer could be developed. These models were used to predict the performance of a 31-liter twin-shaft continuous kneader reactor. The kinetic and torque models accurately predicted the observed performance of the continuous reactor. Due to errors in measuring the actual polymer temperature and the low temperature differences between the polymer and coolant, the overall heat transfer coefficient observed in the continuous reactor was much higher than that predicted by the batch trials. However, the overall heat transfer coefficients for the batch and continuous trials compare well when the basis for the temperature difference was the same.

## Nomenclature

|            |                            |
|------------|----------------------------|
| A          | heat transfer surface area |
| F          | flow rate                  |
| k          | heat transfer coefficient  |
| $\Delta H$ | heat of reaction           |
| M          | torque                     |
| n          | shaft RPM                  |
| Q          | energy rate                |
| t          | residence time             |
| T          | temperature                |
| V          | volume                     |
| X          | conversion                 |

|          |            |
|----------|------------|
| $\Delta$ | difference |
| $\rho$   | density    |
| $\phi$   | fill level |

### Indices:

|       |                  |
|-------|------------------|
| c     | coolant          |
| empty | empty reactor    |
| load  | full reactor     |
| mech  | mechanical       |
| p     | polymer          |
| r     | reactor/reaction |
| spec  | specific         |

## References

1. P. A. Fleury, "Bulk Polymerization of Methyl Methacrylate in a Kneader Reactor", Presented at ANTEC 2006 (2006).

## Key Words

bulk polymerization, kneader reactor, polymerization, high viscosity, heat transfer, torque, scaleup.

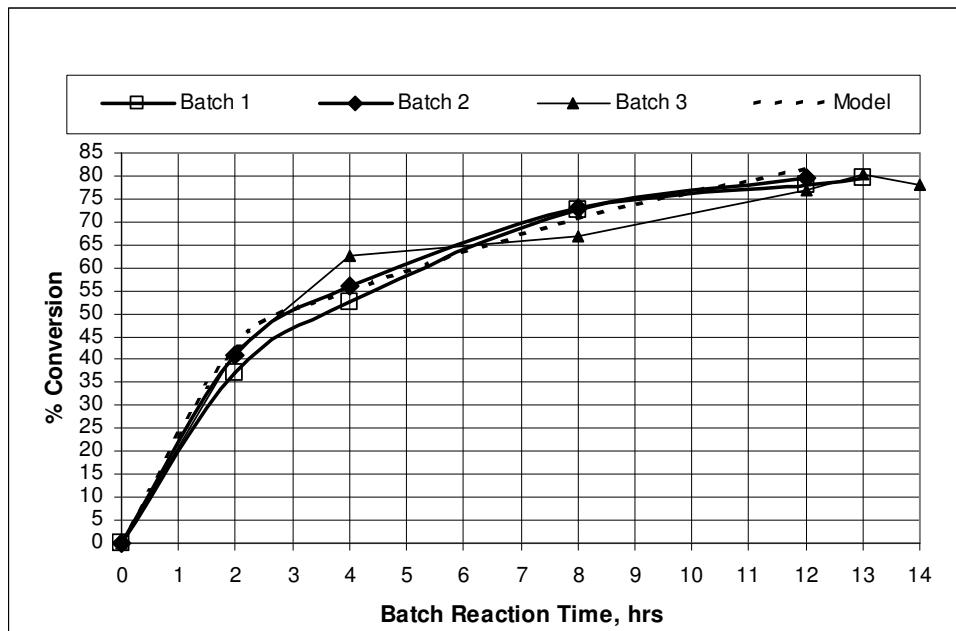


Figure 1: Batch Trial Polymer Conversion

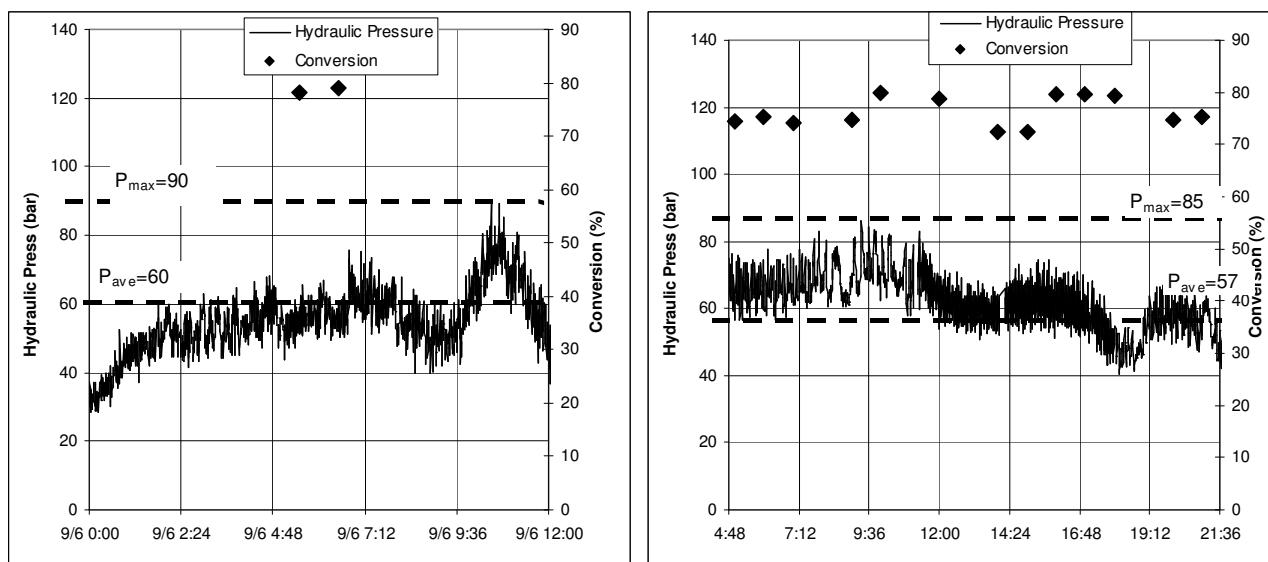


Figure 2 (a and b): Continuous Trial Hydraulic Data and Polymer Conversion for Trials 1 and 2

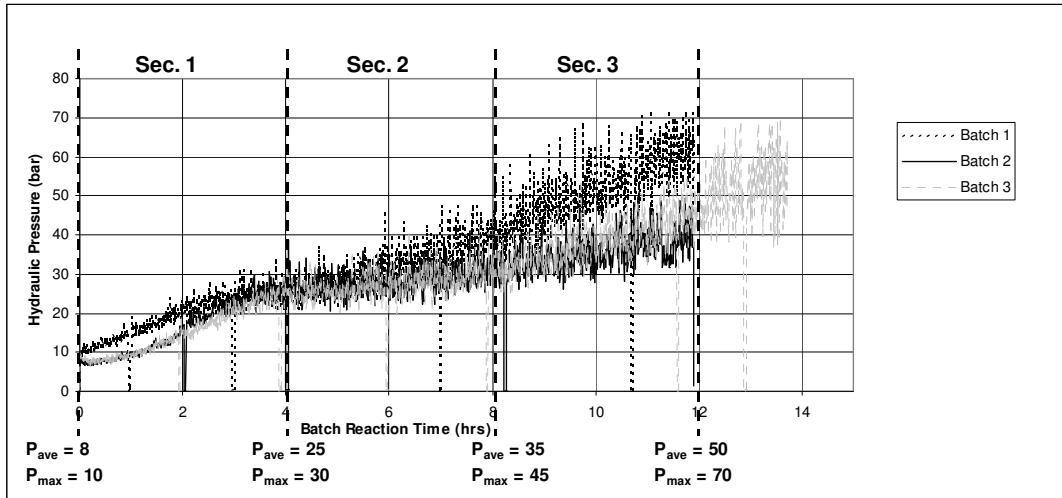


Figure 3: Batch Trial Hydraulic Pressure

|                                       |                     | Section 1 | Section 2 | Section 3 | Total |
|---------------------------------------|---------------------|-----------|-----------|-----------|-------|
| <b>Batch Trials</b>                   |                     |           |           |           |       |
| <b>Average</b>                        | <i>bar</i>          | 17        | 30        | 43        | 30    |
|                                       | <i>Nm/liter</i>     | 18        | 32        | 46        | 32    |
|                                       | <i>Distribution</i> | 19%       | 34%       | 48%       | 100%  |
| <b>Peak</b>                           | <i>bar</i>          | 20        | 38        | 58        | 38    |
|                                       | <i>Nm/liter</i>     | 22        | 40        | 62        | 41    |
|                                       | <i>Distribution</i> | 17%       | 33%       | 50%       | 100%  |
| <b>Continuous Trials*</b>             |                     |           |           |           |       |
| <b>Conti Average (59 bar overall)</b> | <i>Nm/liter</i>     | 5         | 9         | 13        | 26    |
| <b>Conti Peak (85 bar overall)</b>    | <i>Nm/liter</i>     | 7         | 13        | 18        | 38    |

Note: \*distribution of overall torque taken to be the Batch Trial Average Distribution

Table 1: Batch and Continuous Shaft Torque Comparison

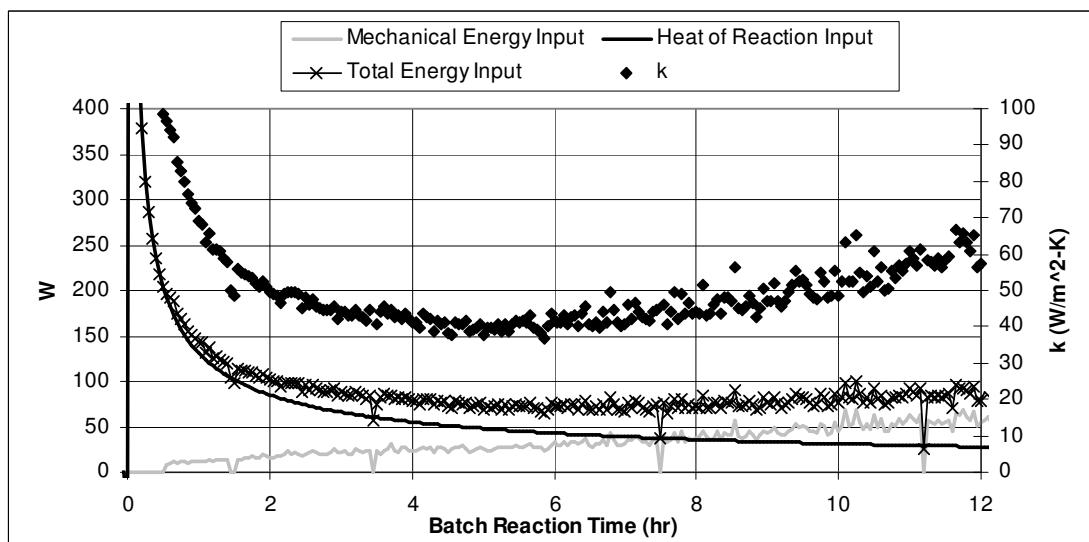


Figure 4: Batch Trial 1 Heat Transfer Calculations