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Developing feed policies to maximize productivity in emulsion polymerization processes[1]

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Abstract

This work deals with maximizing the productivity of our emulsion polymer reactors. Increasing productivity means manufacturing latexes with adequate monomer conversion and final properties, safely, in the shortest possible time. This translates to reduced costs and added capacity. We set out to answer the following questions:

- Are we getting the most productivity from our manufacturing reactors?
- Can we better optimize new and existing products to increase productivity?

The most efficient use of our reactor time requires that we operate at the limit of our heat removal capability (with safety margins). The first step is to quantify what this capability is. One could perform many time consuming studies on each of our manufacturing reactors to identify heat transfer coefficients and rates for each product. Our alternative approach was to use an existing product as a benchmark. Experience had demonstrated that this product was at the limit of our capabilities. This benchmark product was then characterized using reaction calorimetry (Mettler Toledo RC1) and other methods. In this manner, we quickly identified an empirical maximum heat flow "ruler" against which we could evaluate existing and new products. We could now test different feed policies and be assured that we could scale them up economically. These feed policies were identified from calorimetry and pilot plant experiments and by using computer simulation models.

Keywords: Process development; Reaction calorimetry; Emulsion polymerization; Computer modeling; Safety analysis

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1. Introduction

Part of the job of transferring products from the bench-top to manufacturing is to identify processing conditions that not only make the desired product, but are also safe and cost effective. Since reactor time costs money, we want to manufacture the product as quickly as possible. One way to minimize the batch time is to feed the monomer as quickly as possible. However, what does 'as quickly as possible' mean? The faster we feed the monomer, the faster we must remove the heat generated by the reaction. There is a physical limit on how quickly we can remove the heat of polymerization and maintain safe, isothermal, reactor conditions. One can use literature heats of polymerization for each monomer and calculate what the heat generation rate should be, assuming instantaneous reaction. This approach presents us with a few uncertainties:

What is the acceptable heat generation rate, i.e. how fast can we remove the heat from our manufacturing reactors?

What happens if the monomer does not react as fast as you feed it and it accumulates? Does this create an unsafe condition? Does the hold time need to be extended to ensure complete reaction?

This article outlines our approach to deal with these uncertainties using the reaction calorimetry, pilot plant batches, mathematical models and other tools. Firstly, we identified and quantified the acceptable heat removal rate using a benchmark. Then we used this benchmark to test a few products. Finally we went back to refine our benchmark.

1.1. The emulsion polymerization process

A latex is solid polymer particles suspended in water, stabilized by soaps or other surfactants. These polymers are made using a semi batch type process. Water, surfactants and a water phase free radical initiator are added to the reactor. Pre-formed polymer particles (seeds) can also be charged to the reactor. Monomer is added at a controlled rate to the reactor. Monomer must be added slowly enough that the heat of polymerization can be removed from the reactor. Moreover, composition control is accomplished by ensuring that the monomer reacts as fast as it is fed. In this manner the copolymer composition will be the same as the composition of the feed. Particle structure can be built by feeding monomer in several stages, each stage with a different composition The surfactant forms micelles in the water which become swollen with monomer. The initiator decomposes to form free radicals, enters the swollen micelles and polymerization occurs. This forms a polymer particle. Initiator radicals also enter polymer particles to sustain the polymerization. Monomer which is mostly insoluble in water can pool into monomer droplets but is also transported through the water phase to the polymer particles. After the monomer feed is complete, the batch is held to complete the monomer conversion. Other material additions and down stream operations can be performed on the latex.

2. The benchmark for heat removal

In order to ensure processing efficiency while maintaining manufacturing safety we need to quantify acceptable heat removal rates from our manufacturing reactors. The heat removal rate Q, can be given by equation (1) where T_r and T_j are reactor and jacket temperatures, A is the heat transfer area and U is the heat transfer coefficient.

$$Q = UA(T_r - T_j) \tag{1}$$

We can measure the temperatures and the heat transfer area, but U needs to be estimated or measured by experiment. A complete study would find U as a function of fundamental properties such as:

- latex solids, viscosity, composition, etc.
- agitation, rpm, and stirrer geometry
- fouling and reactor cleanliness.

However, for a quick benchmark we've chosen a more empirical approach that uses a product that we currently make. The thought was that we could use this as our benchmark to quantify our maximum heat removal rate. Thus we have the following tasks.

- select a product for a bench mark
- determine if this is a suitable benchmark for maximum heat removal rates
- quantify the heat generation rates for this product

2.1. *Criteria for a bench mark product*

How do we chose a bench mark product? The criteria that we used were:

- It must demonstrate the limit of our manufacturing heat removal
- It is a reasonably typical product
- It has physical properties that give 'some comfort level'

Certainly a benchmark which does not demonstrate the heat removal capability is not useful. However, for our comfort, we also desire a product which is typical of our product line. We also require that the physical properties, like viscosity, give rise to more difficult heat removal than most of our other products. Thus we want our benchmark to be a more conservative estimate of our heat removal capabilities.

2.2. *Is this product a suitable benchmark*

Our manufacturing personnel have indicated that one of our current products is the fastest that we can produce in that temperature control becomes difficult near the end of the batch because of the heat generation rate. This particular product also meets the other two criteria. Several batches of this product, made in our manufacturing facility, were monitored. The process is as follows

1. add water and surfactants to the reactor and heat to the desired temperature
2. add some of the monomer to the reactor as a precharge

3. add the initiator to the reactor
4. feed the remaining monomer at a constant rate over about 65 minutes.
5. after the monomer feed is complete, hold the reaction mixture at temperature to complete the conversion of monomer.

Figure 1 shows the reactor and jacket-outlet temperatures for one of these batches during the feed. The initiator was charged at time zero. We see that the batch temperature remains fairly constant during the feed. However, the jacket temperature falls until it reaches about 8°C where the temperature controller was calling for maximum cooling. This indicates that, at least at the end of the batch, we have reached, or slightly exceeded, the maximum cooling capacity of this reactor. It looks like this product can be used as a benchmark.

2.3. *Quantifying the heat generation rate*

2.3.1. *Reaction Calorimetry*

Reaction calorimetry was performed using the Mettler Toledo RC1 [1]. The experiments were done using the 1 litre glass reactor (MP10). The monomer feed rates were computer controlled (using the RD 10). This reactor performs an on line energy balance during the reaction. Heats and rates of reaction are calculated by monitoring the difference between the reactor and jacket temperatures. Heat flows due to the inflow of monomer (Q_{dos}) is accounted for by knowing the mass flow rate, the heat capacity and the temperature of the feed. The reactor lid was heated to reduce losses. The C_p of the reaction mixture is measured when ever a temperature ramp is implemented, as in heat up and cool down periods. A calibration is performed before and after the reaction. The calibration determines the heat transfer coefficient U by putting a known amount heat flow (about 25W for 15 minutes) into the contents of the reactor, using a calibra-

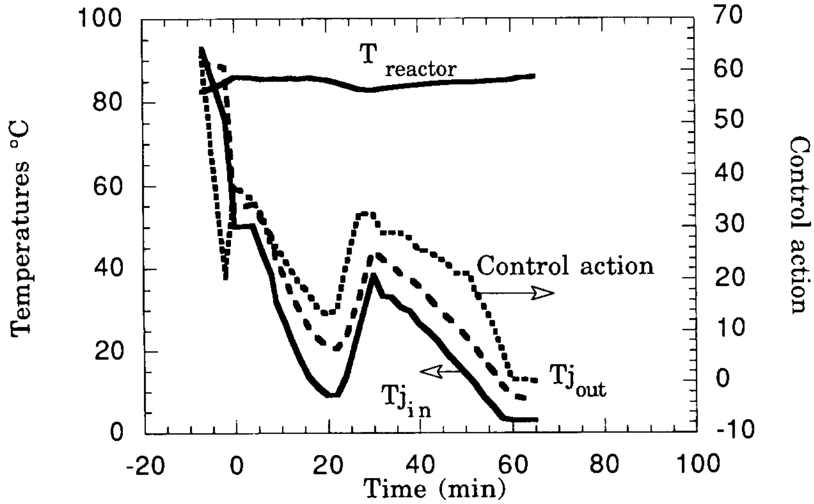

Fig. 1. Temperature profiles for the proposed benchmark produced in our manufacturing reactor.

tion heater, and measuring the change in the jacket temperature (T_j) which is required to maintain a constant reactor temperature (T_r). The heat transfer coefficient is then linearly interpolated between the beginning and the end of the reaction.

2.3.2. *The benchmark*

Several runs of this product were made in the calorimeter to monitor heat flows. Figure 2 shows the normalized heat flows for three batches. The normalized heat flow is defined as the heat flow (W) divided by the mass of the reaction mixture (kg). In this way we can easily compare manufacturing and 1 litre scales. All three batches follow the same profile, with some slight variation. There is an initial spike after the initiator is charged as the monomer precharge is consumed. The monomer addition is accompanied by a large increase in the heat generation rate. The "feed" line in Fig. 2 shows the normalized heat generation rate calculated assuming the monomer reacts as quickly as it is fed. The observed heat generation rate is initially faster than the monomer feed rate, probably due to unreacted precharge. However by the end of the feed the two agree quite closely at a value of about 57 W/kg. This is similar to typical values reported in the literature [2].

The calorimeter experiments show that the maximum normalized heat removal rate occurs near the beginning of the feed (Fig. 2). However, in manufacturing, the maximum cooling was required near the end of the feed (Fig. 1). We know that this product becomes much more viscous as the polymerization proceeds reaching a maximum viscosity near the end of the feed. Heat transfer coefficients generally fall as viscosity increases. Therefore the heat removal is easier early in the batch, when it is less viscous, than it is near the end.

This product appears to be an adequate empirical upper limit on our heat removal rates. The limit on heat removal must be due to the falling heat transfer coefficient near

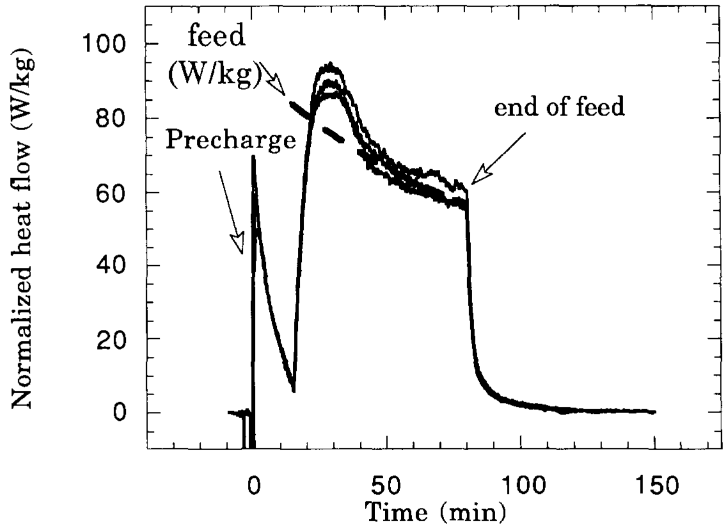

Fig. 2. Heat flows for the proposed benchmark as measured in the calorimeter.

the end of the batch. Heat removal rates might well be much larger for products with lower viscosity and conversely, products with significantly lower reaction temperatures could have lower heat removal rates due to the smaller temperature difference. A more accurate estimate of our heat removal capabilities could be made using the fundamental properties of the system. Nevertheless, this benchmark is a suitable first attempt.

The heat generation rate, calculated from the monomer feed rate is quite similar to that observed in the calorimeter, at least at the end of the feed. It is not as good an approximation near the beginning of the reaction, because of the accumulation of monomer. However, our heat transfer limitations occur near the end of the feed. Therefore we can estimate suitable feed times from literature values of heats of polymerization, and from our benchmark. We only need experiments to confirm our estimates. The following examples show how we've used this methodology to 'optimize' feed rates.

3. Example 1

This example is a product, to be scaled up, with a single monomer feed consisting of a mixture of acrylates. The feed and hold times, specified by our product development group were 120 and 60 minutes respectively. Can we shorten the batch time and how much faster can we go? If we know the heat of polymerization for our monomers we can calculate the feed rate that corresponds to our maximum heat removal rate of 57 W/kg. Unfortunately, we couldn't find a literature value for the heat of polymerization of one of the monomers. Therefore we need to measure this value using the calorimeter. Let's review the objectives of this example.

3.1. *The objectives*

- To measure the heat of polymerization of our monomer mixture, using the calorimeter, so that we can calculate the minimum safe feed time.
- To check our calculations by experimentation.
- To determine the best feed and hold times given the constraints of safe operation, cost and residual monomer levels.
- Compare the calorimeter and pilot plant to verify the results

3.2. *The approach*

The experimental approach is straight forward.

- Run the original process in the pilot plant and replicate the batch in the calorimeter (120 minute feed, 60 minute hold).
- Measure the heat of polymerization. Calculate the minimum feed time, given our heat removal benchmark.
- Run the batch using the new feed rate in the calorimeter to confirm the calculations.
- Run the batch using the new feed rate in the pilot plant to make enough material for performance testing.

3.3. The observations

The first calorimeter batch was simply a replicate of the 50 kg pilot plant batch, 120 minute feed and 60 minute hold. This is an opportunity for us to determine if the results from the calorimeter are transferable to the larger scale. We collected several quenched samples during the course of the pilot plant batch, which were analyzed for unreacted monomer (GC). The conversion of monomer can be calculated from these measurements. The calorimeter calculates the conversion from the heat of polymerization. There is excellent agreement between the two experiments (Fig. 3). Thus we feel confident that we can use the calorimeter responses to predict this behavior at larger scales. The maximum heat evolution rate was about 28 W/kg (Fig. 4). This means that we should be able to feed the monomer over 60 minutes and still meet our 57 W/kg constraint.

$$\left(\frac{28\ \mathrm{W/kg}}{57\ \mathrm{W/kg}}\right)\cdot 120\ \mathrm{min} \approx 59\ \mathrm{min}$$

This is exactly what was tried in the next experiment. In addition, from the measured total heat of polymerization, and literature estimates of the other monomers in the mixture, we were able to calculate the heat of polymerization for the unknown monomer. This means that we can do quick 'back of the envelope' type calculations for other products using this monomer.

The heat generation rates for the 120 and the 60 minute batches are shown in Fig. 4. There are a few important things to notice. Our calculations, based upon the first

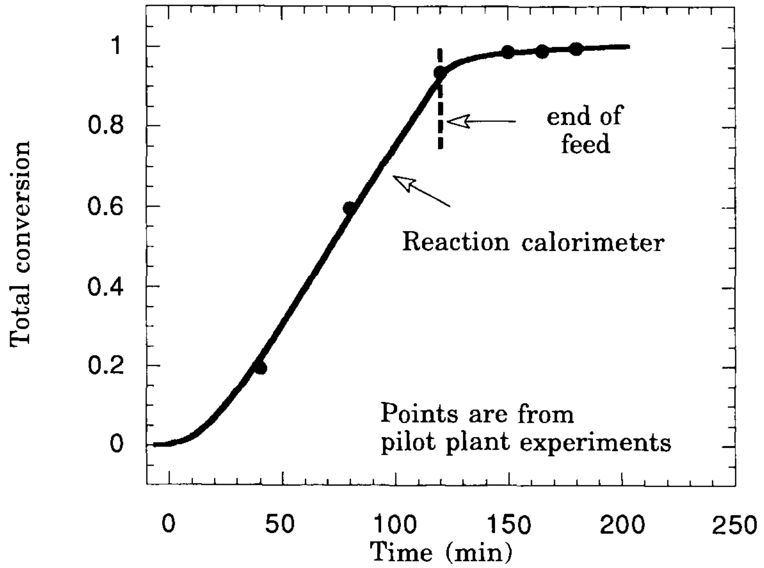

Fig. 3. Conversions as measured by calorimeter and from GC analysis of a 50 kg pilot plant batch.

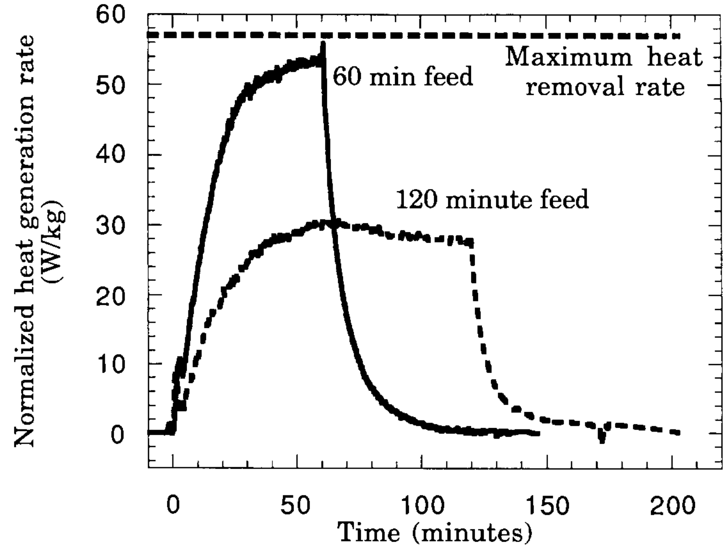

Fig. 4. The measured heat generation rates for the 120 and the 60 minute monomer feeds.

calorimeter experiment, were quite close to what we observed for the 60 minute feed. The maximum rate of polymerization is still limited by the feed rate and this feed rate appears to correspond with our maximum heat removal rate. The reaction for the 60 minute feed, signaled by the fall of the heat flow, appears to be complete much sooner than for the 120 minute feed.

The hold time required to complete the reaction appears to be unchanged (Fig. 5). This means that the reduction in the feed time corresponds to a 60 minute saving in the batch time. Not only does this save money, but it impacts our manufacturing capacity as well. We could make 3 of the 60 minute feed batches in less time than we could make 2 of the 120 minute batches.

3.4. The conclusions from Example 1

- There is excellent agreement between the calorimeter calculations and measurements taken from the pilot plant.
- We should feed the monomer as fast as possible and hold long enough to obtain acceptable free monomer levels. However, we must be concerned that we don't significantly change properties.
- The heat of reaction response from the calorimeter provides an excellent way to develop and confirm maximum heat generation calculations for safe reactor operation. Moreover, we can quickly obtain accurate estimates of the required hold times.

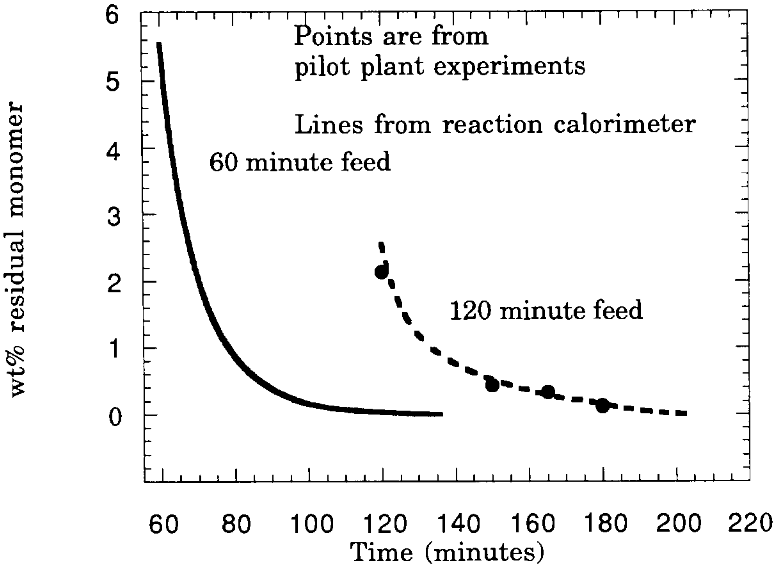

Fig. 5. The monomer levels during the hold time. The lines are calorimeter calculations. The points are GC measurements from the pilot plant batch.

4. Example 2 - calorimeter coupled with mathematical models

This is an example where we couple the calorimeter data with our mathematical simulation model for the polymerization process.

4.2. Computer simulations.

"A process model is a mathematical representation of a production process. Simulation is the use of the model to predict a plant's performance and its economics" [3]. This model is the set of ordinary differential equations resulting from mass balances on the important chemical species [4,5] and our understanding of the chemical and physical mechanisms.

The chemical species include each monomer, polymer produced from each monomer, initiator, water and organic phase radicals, and polymer particles. The partitioning of each species, between the monomer rich, water and polymer rich phases is calculated by assuming thermodynamic equilibrium as described by partition coefficients. Rates of reaction are calculated using propagation rate constants, and reactivity ratios in the usual manner. Energy balances result in differential equations to calculate heat generation rates, reaction temperatures, and cooling water requirements. The molecular weight averages and gel fractions can also be calculated by population balances on the molecular weight moments. A mechanistic model of this form can be used to predict residual monomer levels, copolymer composition, heat loads, particle sizes, molecular structure, etc., as functions of time, as influenced by feed rates, temperatures and like. The model becomes a repository of our knowledge of the system, the simulation is the retrieval method. Comparison with observation allows us to test our hypotheses about the mechanism. "... the mathematical model is the best way to find out what one does not know about a process" [6].

The 'heart' of the model is Eq. 2.

$$Rp = k_p \bar{n}[M]\frac{N_p}{N_a}V_w \tag{2}$$

where k_p is the propagation rate constant, $\bar{n}$ is the average number of radicals per particle, $[M]$ is the monomer concentration, N_p is the number of particles, N_a is Avagadro's number and V_w is the volume of water. The monomer concentration is determined by the balance between the feed rate and the reaction rate.

The differential and algebraic equations were programmed in FORTRAN and are solved numerically using an version of Gears method (LSODE) [7]. The code was compiled for the Power Macintosh using Language Systems™ LS FORTRAN v1.0. The program takes about 3–5 minutes to run.

The modeling assumptions, for this example, are as follows:

- this is a 0-1 system, that is radicals terminate upon entry to particles with a radical.
- the polymerization is seeded, i.e. all the polymer particles are present at the beginning and there is no nucleation. The seed is mono-dispersed.

4.3. *The example recipe*

The monomer is fed in two stages. The first feed is mostly monomer 1 while the second feed is a mixture of monomers 1, 2 and 3. There is a hold period between the feeds.

4.4. *Matching the model and the recipe*

Firstly, we need to make sure that the model can accurately describe the rate of reaction. Most of the model parameters could be found in the literature but some needed to be estimated from the experimental data. These data were collected from pilot plant runs (residual monomer composition and particle diameter) and from the calorimeter (rates of polymerization and heat generation). Fig. 6 compares the model and the experimental particle size data. The particle diameters were measured by capillary hydrodynamic fractionation (CHDF), and the number average diameters are used here. The model accounts for the particle diameter quite well.

The residual monomer levels are compared in Fig. 7. The model quite accurately calculates the residual monomer 1 level. The model tends to under predict the amounts of residual monomers 2 and 3.

However the most interesting comparison is the normalized heat generation rate (Fig. 8). This gives us the most accurate measure of the rate of reaction. The model generates a curve that is quite similar to that observed in the calorimeter. Specifically the rate increases during the first feed. Moreover, the trend to a higher rate during the second feed is predicted as well.

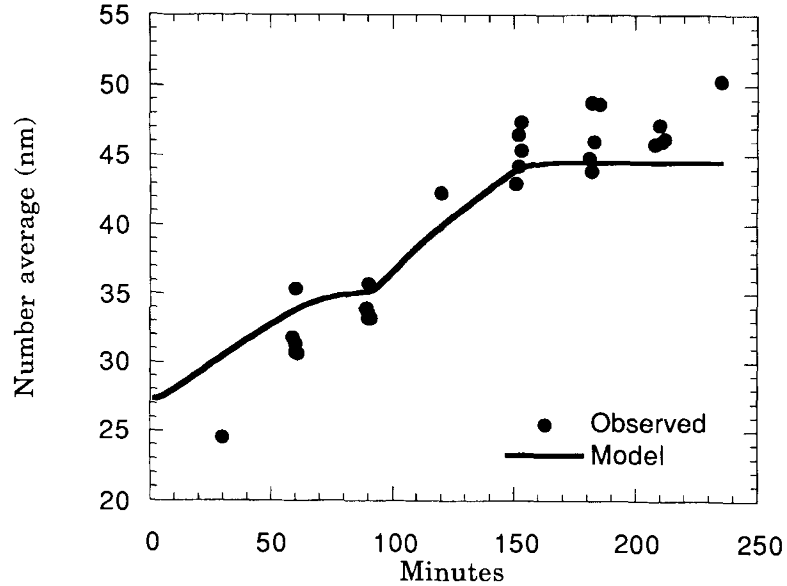

Fig. 6. The observed and calculated particle diameters.

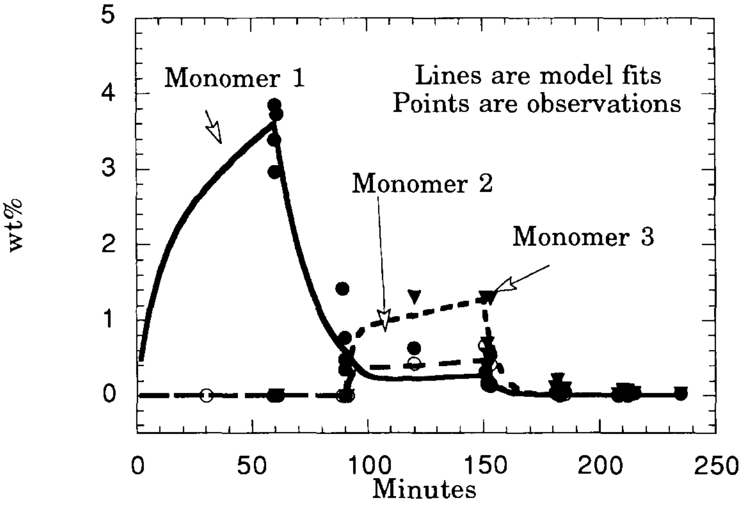

Fig. 7. Residual monomer levels measured for the pilot plant batches and the model fits.

4.5. *Using the model to determine feed policies*

We can use the mathematical model as a tool to try some 'what if' type *experimentation*. We can quickly screen feed scenarios to identify the most cost effective policies. Then we can calculate what the effects of these policies would be on the polymer micro

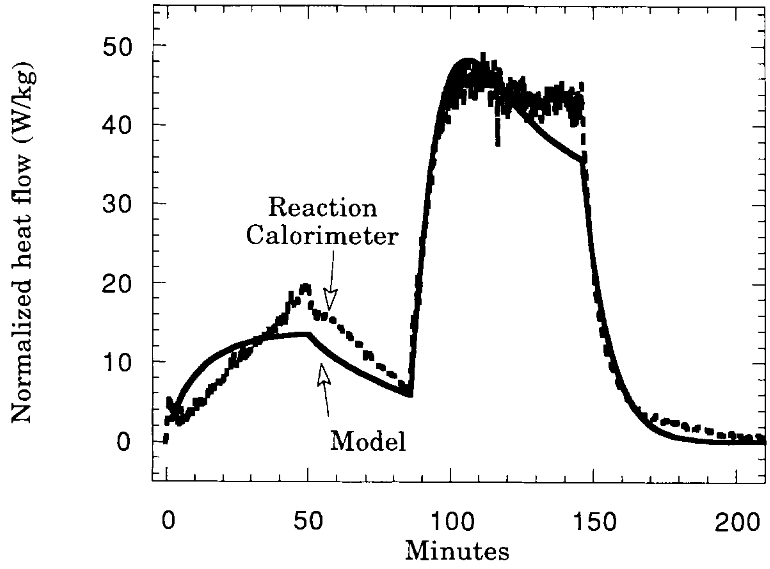

Fig. 8. The normalized heat generation rate as calculated by the model and measured in the calorimeter.

structure. The cost savings is another result of this technique, but its importance would be a derivative of the reactor time or processing time. What is important is that we can use models and simulations to replace sets of screening experiments. We can probe those 'wild ideas' to see if they might work, and then save some valuable time and resources by running only the confirming experiments for the models that show improvement.

A mathematical model, in conjunction with results from the calorimeter, was used to develop a more cost effective feed policy. Several simulations were run to test the influence of the feed and hold times on the heat loads and residual monomer levels. Feed and hold times were then selected based upon manufacturing heat removal capabilities and the rate of reaction as quantified by the model. This example is presented primarily to illustrate how we can use simulation models (as validated by the calorimeter and other reactors) to quickly probe our ideas. The simulations, including complete analysis of the results, can be performed in about half a day. This is appreciably faster than performing the corresponding experiments and analyses.

Fig. 9 shows the predicted heat generation rate plot. The limit of heat removal, in our production reactors, is shown by the broken line at 57 W/kg.

Can we use the simulation model to suggest a more cost effective process?

4.6. *Reducing the first feed time*

We have determined that we can accommodate a heat flow 57 W/kg in our manufacturing reactors. Lets compare this batch to our benchmark. The heat load of

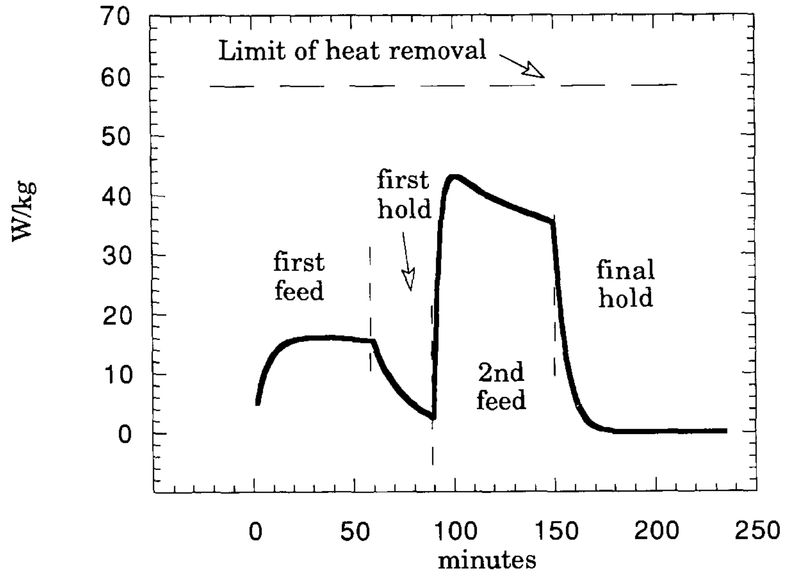

Fig. 9. The predicted heat flow rates for the base case recipe.

the first feed corresponds to about 20 W/kg. A simple calculation shows that we could shorten this feed to about 20 minutes and still remove the heat.

$$\left(\frac{20\ \mathrm{W/kg}}{57\ \mathrm{W/kg}}\right)\cdot 60\ \mathrm{min} = 21\ \mathrm{min}$$

This is assuming that the reaction is feed rate limited. Does monomer 1 react fast enough to reach this maximum heat load? The very gradual fall in the heat flow after the end of the first feed suggests that the rate of reaction might not be feed rate limited. To test the extreme case we ran a simulation were we precharged the entire first feed (Fig. 10). That is we added all the first feed monomer to the reactor before we added the initiator. The maximum heat load was calculated to be only about 44 W/kg. Therefore the rate of reaction is not limited by the feed rate but by the propagation rate of the monomer. The precharge represents the minimum possible feed time (i.e. zero minutes).

Now, if we precharge the first feed the question becomes; how long should we hold it before we start the second feed? Comparison of the monomer 1 level of the base case at the start of the second feed indicates that we should hold for about 70 minutes (Fig. 11). The base case started the second feed after 90 minutes (60 minute first feed, 30 minute hold) so we have a 20 minute time saving by using the precharge.

4.6.1. Is this precharge safe?

We are allowing a significant amount of monomer to accumulate in the reactor by using this precharge strategy. Does this pose a safety problem? One way to quantify the

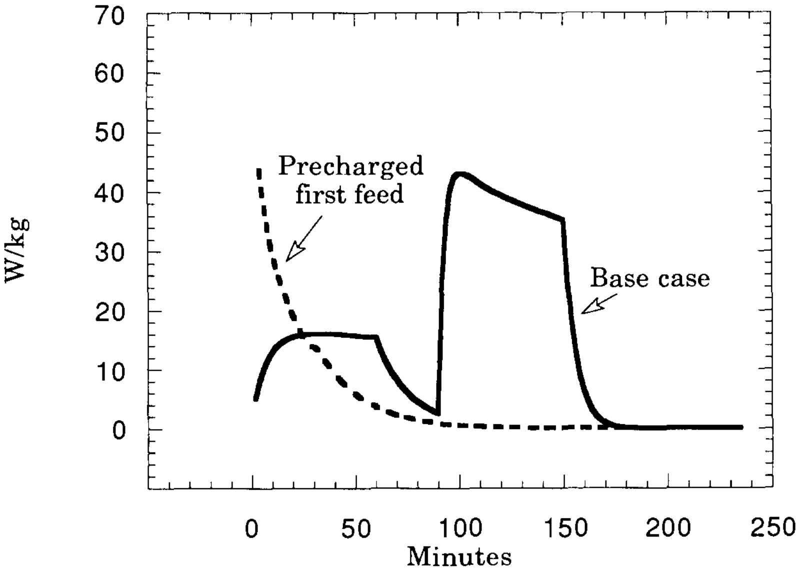

Fig. 10. The simulated normalized heat flow rate for the base case and the precharged first feed (second feed omitted from precharge simulation).

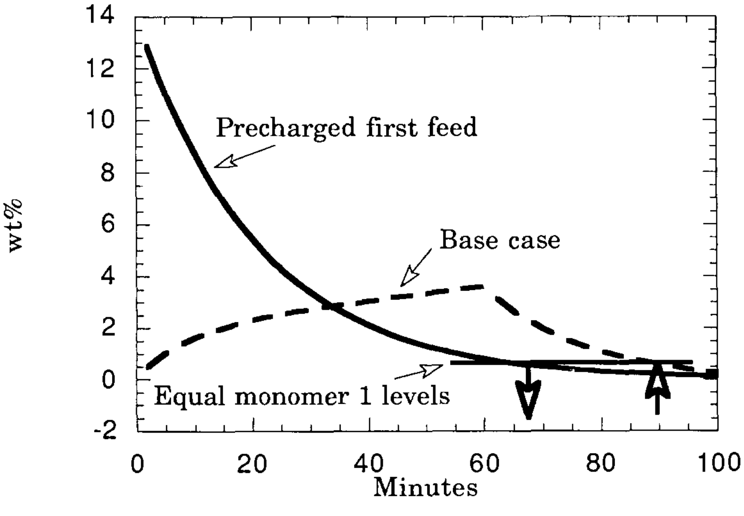

Fig. 11. The monomer 1 level as a function of time for the base case and for a precharge of the first feed.

risk is to calculate the maximum temperature rise (T_{max}) for a worst case failure. That is, just how hot could the batch get? In this example a worst case failure would be a total loss of cooling immediately after the initiator addition. Then the entire precharge of monomer would react under adiabatic conditions causing an increase in the reaction temperature. We can calculate what this temperature rise would be and then make a judgment as to the consequences. The maximum temperature is calculated from

$$T_{\max} = T_r + \Delta T_a$$

where ΔT_a is the adiabatic temperature rise and is calculated by

$$\Delta T_a = \frac{Q_{\text{rxn}}}{C_p \cdot m}$$

C_p is the heat capacity of the reaction mixture and m is the mass of the reaction mixture. Q_{rxn} is the total heat evolved if the polymerization goes to completion. This can be found from the area under the Q vs. t curves from the calorimeter or using literature values for the heat of polymerization of this particular monomer mixture. The heat capacity of the reaction mixture is calculated by the calorimeter but can also be measured by other methods like DSC. For this case, the entire first feed reacting under adiabatic conditions, we calculate that $\Delta T_a = 16°\text{C}$. Therefore, since our reaction temperature is about 75–80°C the maximum reactor temperature is 90–95°C. This temperature is less than the boiling point of any component in the reactor (including water). Moreover none of the components will dangerously decompose at these temporaries. An adiabatic run away would not result in an excessive pressure build up or other unsafe condition. We can conclude that the precharge poses no safety problems.

4.7. *Reducing the second feed time*

We can then run the simulation where we precharge the first feed, hold 70 minutes and then start the second feed (in order to keep this article as brief as possible, these simulation results are not shown.) The maximum heat generation rate, during the second feed is found to be only 40 W/kg. This means that we can reduce the second feed time to about

$$\left(\frac{40\ \text{W/kg}}{57\ \text{W/kg}}\right) \cdot 60\ \text{min} = 42\,\text{min}$$

and still maintain less than 57 W/kg for the maximum normalized heat load. Fig. 12 shows the simulation using the precharge and the shortened second feed (40 min.) as compared to the base case. We are still within our heat load constraint.

4.8. *The final hold*

Since we're feeding the second monomer mix over a shorter time, we might expect the hold time required to reach a certain residual monomer level to change. The model simulations predict that comparable residual monomer levels can be reached using the same hold time (within 10 minutes).

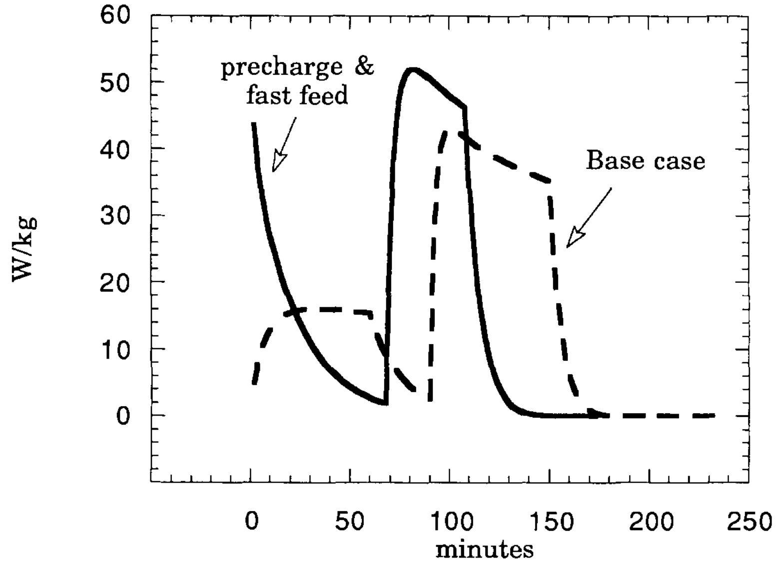

Fig. 12 The heat load requirements for the base case and for the new feed policy.

4.9. Summary of the new process times

A summary of the process times is given in Table 1.

This new process results in a 20% reduction in the batch time, about 40 minutes.

4.10. Does it work?

The question remains: does the change in feed policy affect the performance of the polymer? The performance is most likely influenced by the copolymer composition and the particle size. The particle size is determined by the seed and we can calculate the copolymer composition for each feed policy. In fact, the most sensitive measure is the instantaneous copolymer composition (ICC), that is, the composition of the polymer that is being formed at any moment in time. When we plot the ICC against the percent

Table 1
Summary of processing times for example 2

Time for each step (minutes)	Base case	New process
precharge hold	0	70
first feed	60	0
first hold	30	0
second feed	60	40
final hold	60	60
total time	210	170

non volatile (%NV) (Fig. 13) we see that there is not very much difference between the two feed policies. The %NV is used since the feed times are different between the two policies. Since the ICC is quite similar we might expect the performance to be similar. However, we should run the experiment to confirm performance.

A 40 kg batch was made in the pilot plant which ran quite well with no temperature control difficulties. Several quenched samples were collected to observe the residual monomer and particle size profiles (Fig. 14 and 15). We must point out that the lines are model *predictions*, not model fits. The significance of this is that we used the model to *extrapolate* to a region outside the experimental area used to fit the model parameters. Nevertheless the agreement is quite good. The model predictions are probably within batch to batch variation demonstrated in Figs. 6 and 7. The performance of this latex, in its intended application, was measured and compared to several other replicates of this latex using the standard conditions. The batch with the shortened process time has properties well within the batch to batch variation.

4.11. Conclusions for example 2

- The entire first feed could be precharged without compromising temperature control or safety in the reactor. A hold time of 70 minutes is required to reach conversion levels comparable with the base case.
- The second feed could be reduced from 60 to 40 minutes.
- Thus the precharge and short feed results in an overall time savings of about 40 minutes.
- Even though the model was used to extrapolate to process conditions outside the region of fit, the model predictions agreed quite well with an actual the pilot plant batch.

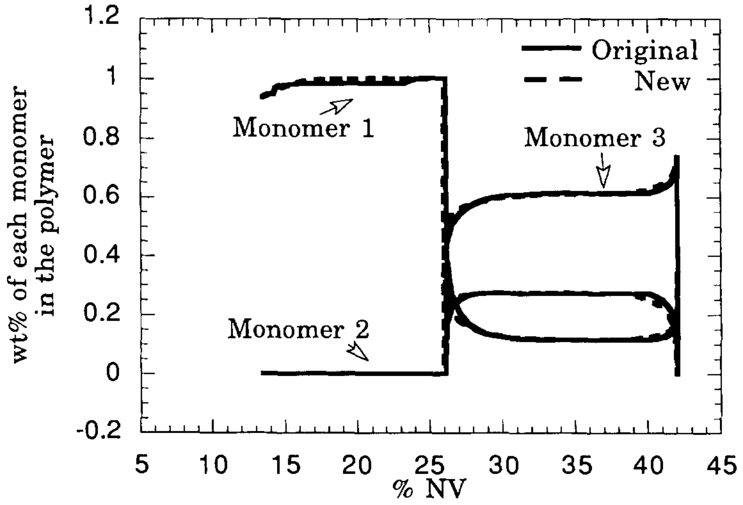

Fig. 13. The instantaneous copolymer composition for each feed policy.

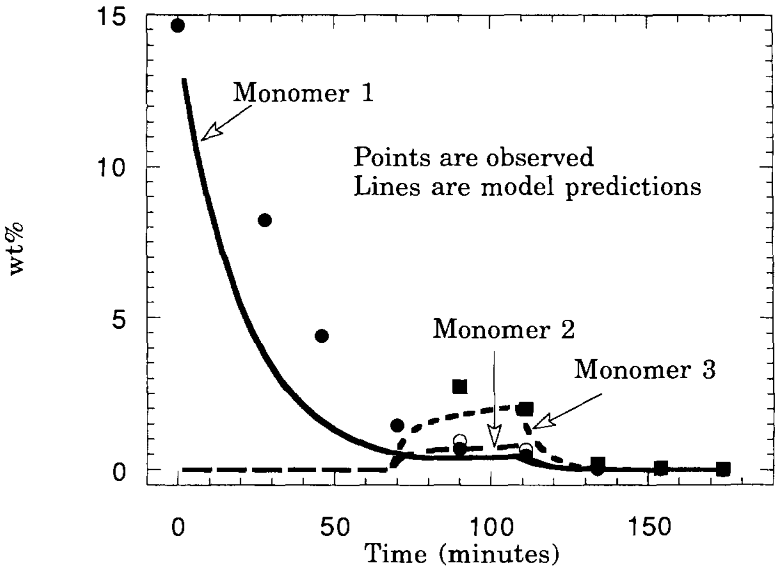

Fig. 14. The observed and predicted residual monomer levels for the new feed policy batch.

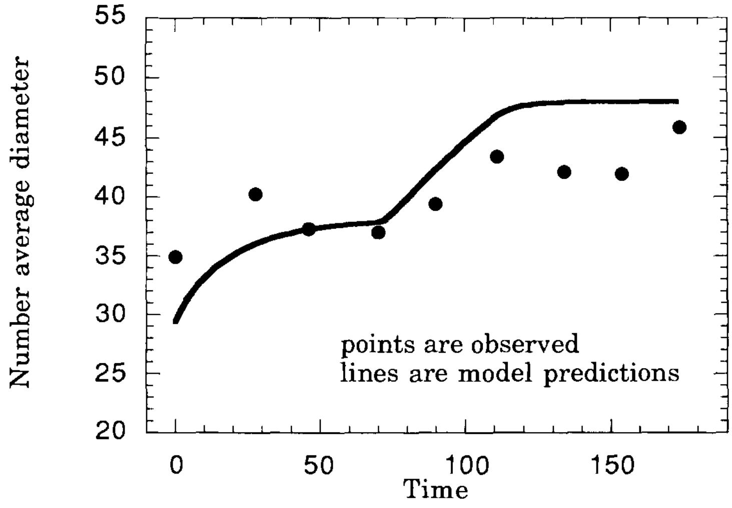

Fig. 15. The observed and predicted particle diameters for the new feed policy batch.

- The product performed well
- The mathematical model (coupled with the calorimeter and other experiments) proved invaluable for screening experiments to quickly determine promising processing routes.

5. Redefining the benchmark - the next iteration

We have chosen currently manufactured product to be our empirical benchmark for maximum heat removal rate. In the first section we acknowledged that we could probably get a more precise estimate. This section outlines some of our work in this regard. Moreover this section demonstrates the excellent agreement between the calorimeter and manufacturing reactor and how the heat transfer coefficient correlates well with theory. These two observations should help us to accurately scale from the 1 litre calorimeter to the manufacturing reactors. Moreover our estimates of the heat transfer coefficients enable us to calculate an 'optimal' feed policy to best use the cooling capacity of the reactor.

5.1. *The objectives*

- To observe and quantify the heat generation and transfer characteristics of our manufacturing reactor and compare these observations with those from the calorimeter.
- To relate the heat transfer coefficients to physical properties of the latex.
- To calculate an optimum feed profile for the benchmark process.

5.2. *The observations*

This section is based on the observation of a batch of our benchmark product in one of our manufacturing reactors. The reactor and jacket temperatures, heat transfer coefficients, heat transfer areas and mass flows were recorded roughly every two minutes. The heat transfer coefficients are estimated by the control software from an energy balance on the reactor and cooling jacket. Samples were withdrawn from the reactor during the monomer feed and analyzed for %NV, density and viscosity.

5.3. *Comparison with the calorimeter*

We can calculate the normalized heat generation rate from manufacturing reactor from an energy balance on the cooling water. Fig. 16 demonstrates that the normalized heat generation rates as measured in the calorimeter and in the manufacturing reactor are quite comparable.

5.4. *Heat transfer coefficients*

The heat transfer coefficient (U) is estimated by the control software based on energy balances on the reactor and jacket. The heat transfer coefficient falls with the time (Fig. 17).

The heat removal rate, for constant reaction temperature is given by:

$$Q_{\mathrm{rxn}} = Q_{\mathrm{removed}} = UA(T_{\mathrm{r}} - T_{\mathrm{j}}) \tag{3}$$

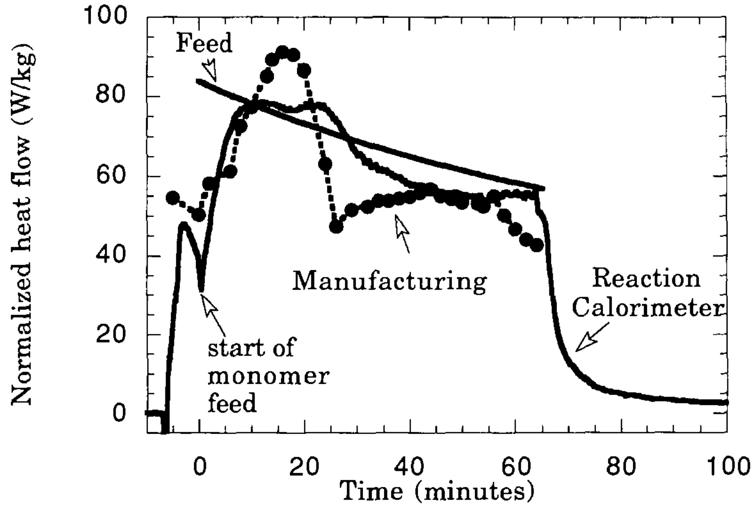

Fig. 16. The normalized heat generation rates from the calorimeter and manufacturing reactor.

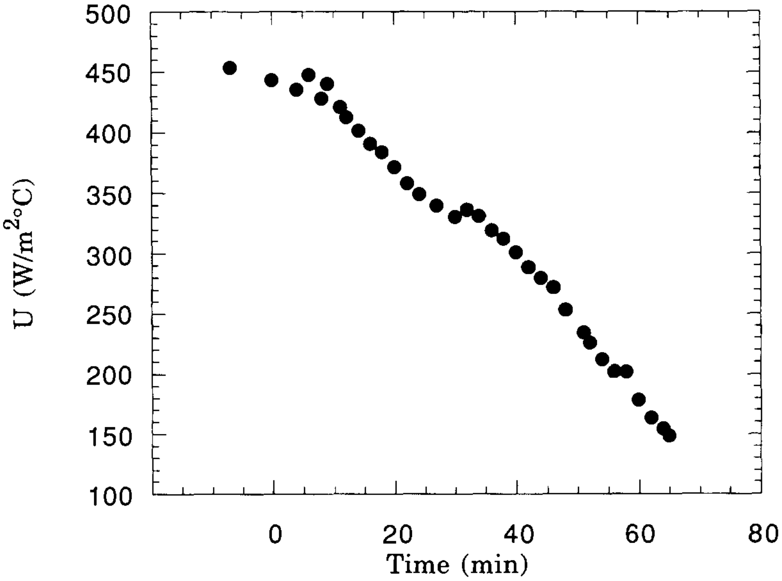

Fig. 17. The calculated heat transfer coefficient (U) for manufacturing reactor.

The monomer feed is constant and thus the heat load (Q_{removed}) on the reactor is fairly constant. The heat transfer area (A) increases as the reactor contents increase. Nevertheless the cooling demand increases ($T_r - T_j$) because of the falling U.

If we can relate the heat transfer coefficient to the fundamental properties of the system, we should be able to predict heat transfer rates. Overall heat transfer coefficients are calculated by adding the resistances to heat transfer across each transfer area, i.e.

$$\frac{1}{U}=\frac{1}{hj}+\frac{\mathrm{d}w}{kw}+\frac{1}{hf}=\frac{1}{U_\mathrm{r}}+\frac{1}{hf} \tag{4}$$

where $1/hj$ and $1/hf$ are thermal resistances to heat transfer through the reactor jacket and reactor contents, respectively, dw is the reactor wall thickness and kw is the thermal conductivity of the wall material. $1/U_\mathrm{r}$ is a group that accounts for all thermal resistances that are not functions of the fluid properties of the contents, and hf accounts for the latex in the reactor. It can be shown [8] that for polymers hf is largely a function of the fluid viscosity such that

$$\frac{1}{U}=\frac{1}{U_\mathrm{r}}+\frac{1}{hf}=\frac{1}{U_\mathrm{r}}+\alpha\mu^{1/3} \tag{5}$$

where μ is the latex viscosity and α is a proportionality constant. This means that if we were able to plot $1/U$ vs. $\mu^{1/3}$ we should get a straight line with intercept $1/U_\mathrm{r}$ and slope α. This approach is a simplification of the Wilson method [9]. Well, we sampled the benchmark made in the manufacturing reactor and measured the viscosity (Brookfield spindle # 2 at 60 rpm at 25°C). We also used these samples to measure the heat transfer coefficients in the calorimeter at 25°C. Fig. 18 shows that Eq. 5 gives an excellent representation of the relationship between viscosity and heat transfer coefficient.

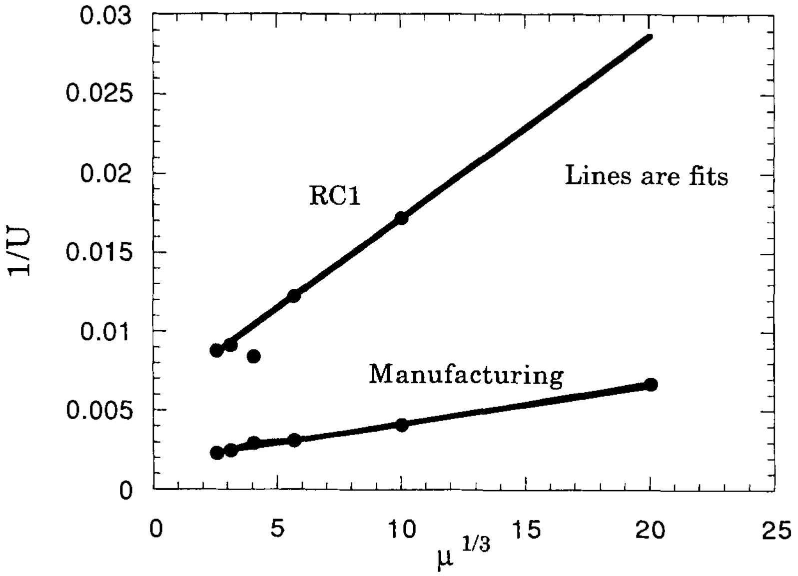

Fig. 18. The heat transfer coefficient(U) in manufacturing reactor and calorimeter as a function of viscosity (μ).

It is reasonable that the heat transfer coefficient (U_r) should be much larger for manufacturing reactor than the calorimeter because stainless steel has a much higher thermal conductivity than does glass.

5.5. How can we use these heat transfer coefficients?

A closer examination of these data shows two things, firstly we only use the maximum cooling at the end of the batch, and secondly, we still have a small temperature excursion near the end of the feed. Can we adjust the monomer feed to utilize our cooling capacity and avoid this temperature rise? Since we now have an estimate of U and A over the feed time, we can calculate the heat removal rates based on equation 1. If we specify that the cooling water temperature is fixed near the minimum, then we can calculate the maximum heat removal rate. Using the heat of reaction of the monomer we can convert the heat removal rate to a feed rate. Fig. 19 shows this 'optimal' feed rate. The new feed rate is higher at the beginning and falls to a level near the current feed rate. The feed time can be reduced by 20%. Verifying these predictions by experiment is under way.

This is the sort of analysis we can do with our new products. We can estimate U from the viscosity of the latex, during the polymerization, assuming that α is similar for this product, or estimating it from calorimeter data. Then using this information we can calculate more ideal monomer feed profiles that take into account the changing heat transfer coefficient, reaction temperatures.

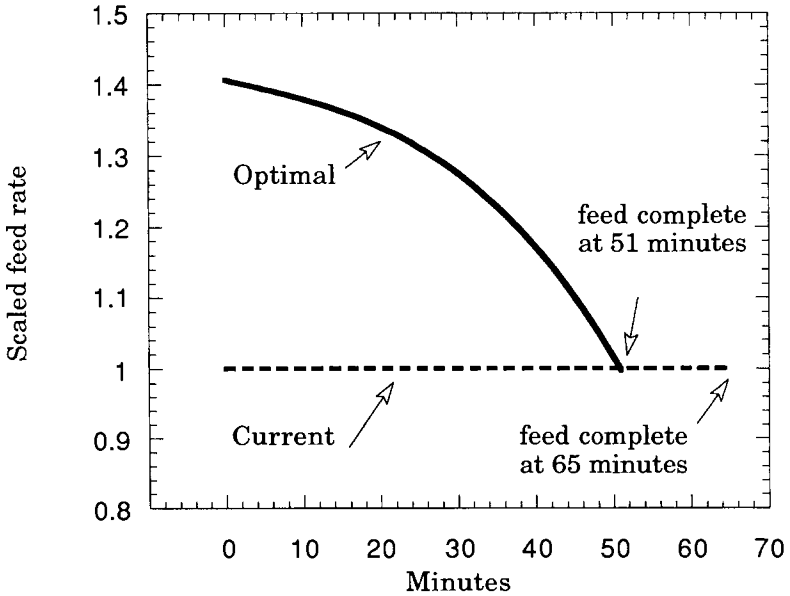

Fig. 19. Optimal feed rate based upon constant heat removal rates.

6. Conclusions

Using a current product is a very good way to get a quick benchmark for maximum heat removal capabilities.

Reaction calorimetry and simulation models are excellent tools to identify and feed policies. The normalized heat generation rate curves for the calorimeter quite nicely represent those observed in manufacturing reactor. Thus measurements from the calorimeter can be directly used for scale up to manufacturing.

Closer observation of the benchmark product canlead to more useful estimates of maximum heat removal rates by using the physical properties of the product and reactors. Moreover, it can suggest improved feed policies.

The heat transfer coefficient correlates very well with latex viscosity according to the Wilson method. Thus we should be able to better estimate the heat load from the physical properties of the latex and the reactor. An ‘optimal’ feed profile can be found based upon the estimates of the heat transfer coefficients which shortens the batch time and could improve temperature control.

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References

[1] Mettler Toledo AG CH-8606 Greifensee, Switzerland
[2] R.N. Landau Automated Laboratory Reactors and Calorimeters Whitehouse Station Reprographics Merck & Co. Whitehouse Station, NJ. p. 4
[3] J.H. Krieger Process simulation seen as pivotal in corporate information flow C & EN March 27, 1995
[4] A.E. Hamielec et al. ‘Multicomponent Free-Radical Polymerization in Batch, Semibatch and Continuous Reactors‘, Makromol. Chem. Macromol. Symp. 10/11 521–570 (1987)
[5] T.O. Broadhead et al. ‘Dynamic Modeling of the Batch Semibatch and Continuous Production of Styrene/Butadiene Copolymers by Emulsion Polymerization‘, Makromol. Chem. Suppl. 10/11 105–128 (1985)
[6] A. Penlidis Polymer reaction engineering: From reaction kinetics to polymer reactor control, Can. J. Chem. Eng. 72 , 385–391, 1994
[7] A.C. Hindmarsh OPEPAC, a systematized collection of ODE solvers in Scientific Computing, R.S. Stepleman ed. North-Holland, Amsterdam (1983) Vol. 1 of IMACS transactions on scientific computation) pp. 55–64
[8] R.M. Machado Estimation of heat transfer coefficients in high viscosity systems for the RC1 Air Products and Chemicals (1992)
[9] E.E. Wilson A basis of rational design for the heat transfer apparatus Trans. Am. Soc. 37 p. 47